47th ANNUAL MEETING OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVI MAY 1951 No. 5

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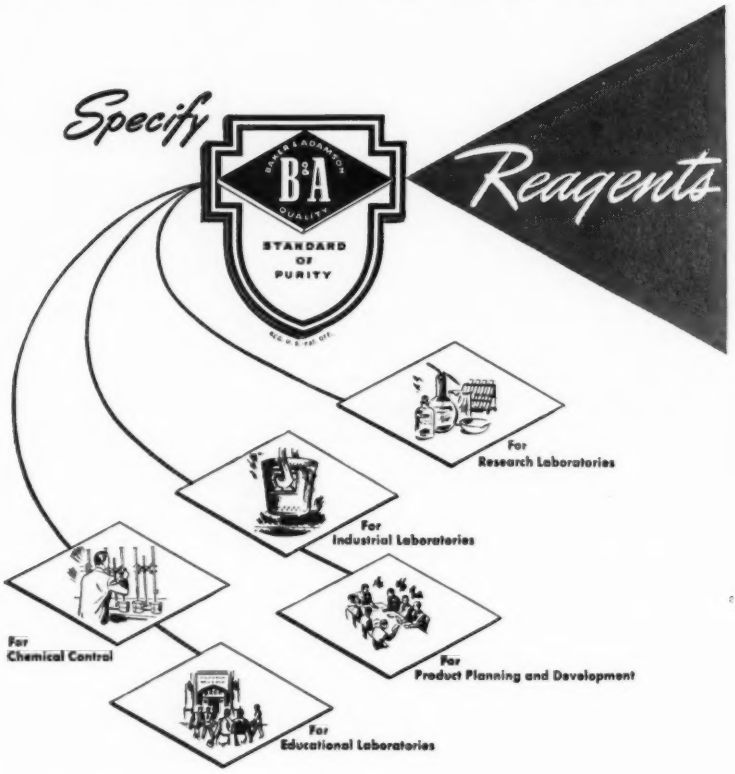

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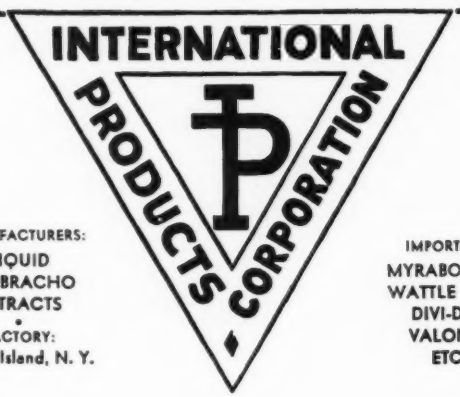

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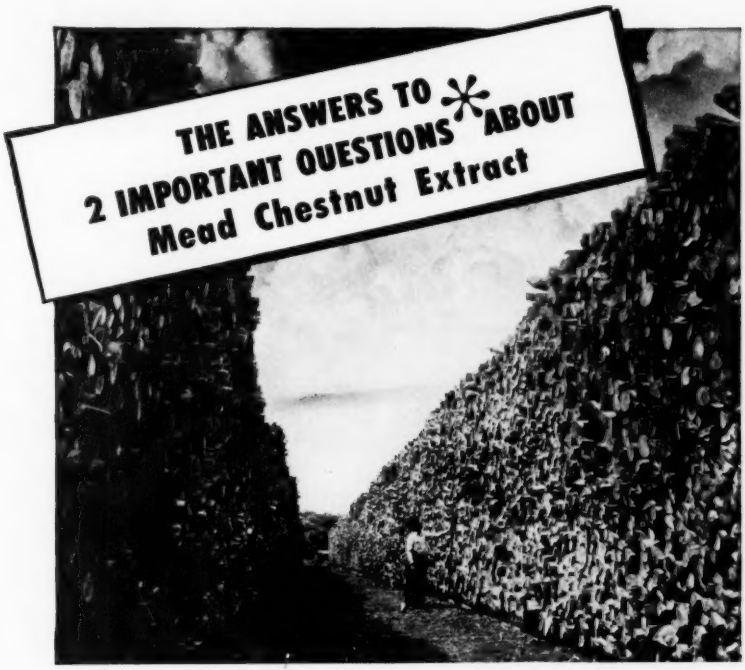

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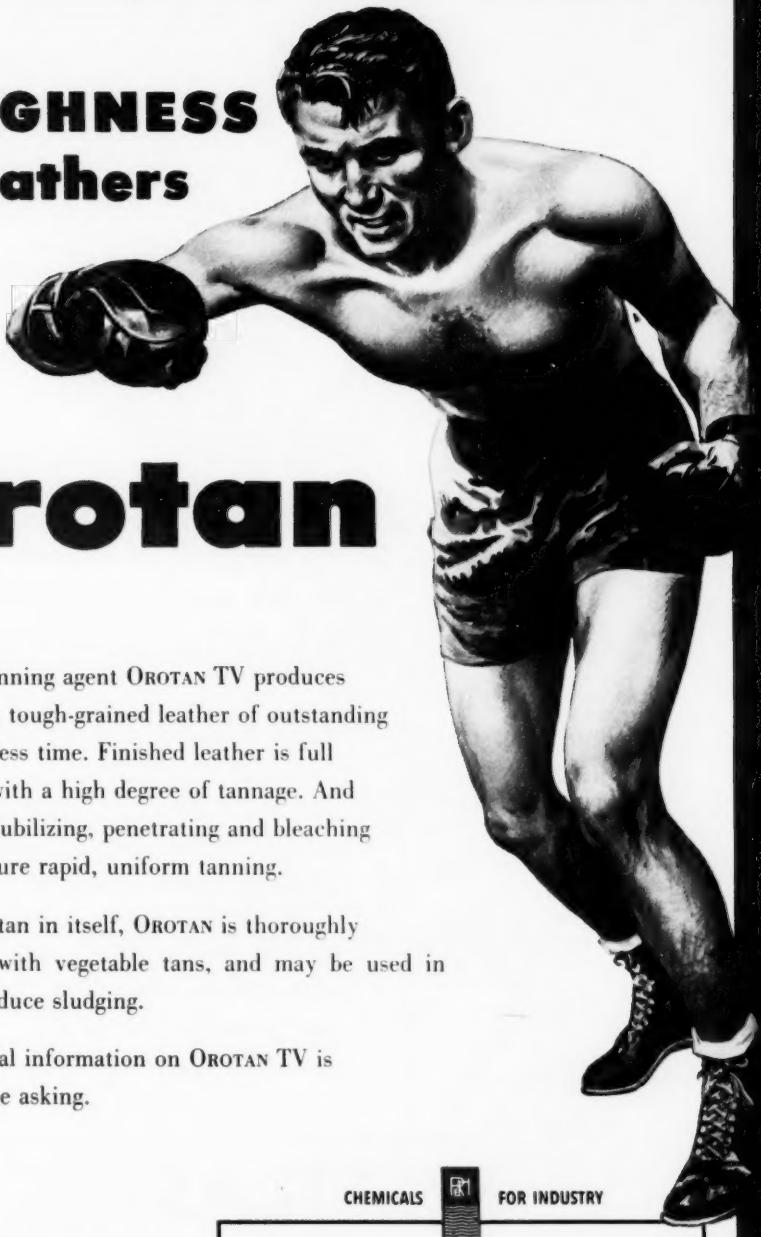

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ANALYSIS

Na_2S	60 to 62%
NaCl	1.5% Max.
Other Na Salts	2.0% Max.
Fe	8 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	35% Min.

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Mol. Wt. 56.1
M.P. . . . . 55°C

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ANALYSIS

NaSH	70 to 72%
Na_2S	2.5% Max.
NaCl	0.8% Max.
Na_2SO_3 and $NaHCO_3$	0.4% Max.
Fe	5 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	28 to 26%

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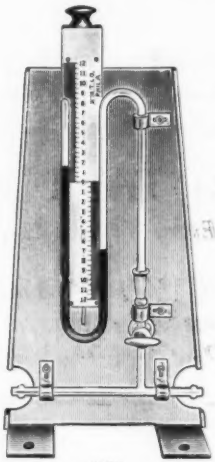

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SECRETARY'S NOTICE

The volumes of the Journal of the late Ade Winheim are offered for sale. They consist of: 1931–1935 to 1948 inclusive, bound, and 1949–1950 unbound. They are appraised at $150.00 for the lot. Offers will be received by the Secretary.

FRED O'FLAHERTY

CORRECTION

In the proposed method for copper determination, [See *This Jour.* 47, 4 (1951)], xanthate should replace the word xanthates. One gram Potassium ethyl xanthate should be dissolved in 1000 ml. of water instead of the 100 ml. specified in the printed text.

F. O'Flaherty, Secy.

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ANNUAL MEETING ANNOUNCEMENT

The Forty-Seventh Annual Meeting of the American Leather Chemists Association will be held from Monday June 11th through Wednesday, June 13th at The Griswold, Groton, Connecticut.

On Sunday June 10th, both afternoon and evening, the various technical committees of the Association will meet, and those who are members of active committees are urged to include these meetings in their plans. In addition to the scheduled committee meetings, five full technical sessions will be held during the three days of the meeting. (Morning and afternoon sessions on Monday and Tuesday, and a morning session on Wednesday.)

An important business meeting will be held by Dr. Koppenhoefer at the beginning of the Monday morning session for the discussion and vote by the membership and pertinent items.

This year the annual banquet is being scheduled for Wednesday evening, the third day of the meeting, and follows an afternoon of recreation. This has been done to stimulate attendance through the entire technical program, and it is hoped that the membership will cooperate. For those who do not plan to participate in the Golf Tournament, the Wednesday afternoon will present an excellent opportunity for worthwhile discussion.

The Technical Papers include

1) Symposia on Advances in Leather Technology. *Panel Chairman*, E. R. Theis.
2) The Leather Chemist Analyzes His Industry, *by* K. E. Bell.
3) Some Notes on the Mixing of Tan Yard and Retan Liquors Using Various Vegetable Extracts, *by* S. K. Johnson.
4) Effects of Tannery Processes on the Electron Microscopic Appearance of Bovine Hide Collagen, *by* R. Boraskey and J. S. Rogers.
5) Sources of Variance in the Specification Properties of Army Retan Upper Leather, *by* R. M. Lollar.
6) Some Data on Dry Shrink Temperature of Collagen, *by* W. T. Roddy.
7) Practical Methods of Assessing Significant Improvements in the Quality of Insole Leather, *by* S. S. Kremen.
8) Enzyme Evaluation by Viscosity Reduction, *by* J. Nickerson.
9) The Determination of Acidic and Basic Amino Acids by a Chromatographic Method, *by* J. M. Cassel.
10) The Sampling of Upper Leather, *by* C. W. Mann.
11) The Leather Chemist of 1951, *by* H. G. Turley.
12) The Effect of Splitting on the Strength of Upper Leather, *by* J. R. Kanagy.
13) The Application of Statistics in the Tanning Laboratory, *by* F. D. Thayer, Jr.
14) Recent Findings on Tanning Properties of Lignosulfonates, *by* J. R. Salvesen.

15) Factors Influencing Lignin Sulfonate Absorption by Hide Powder, *by* H. B. MARSHALL.
16) Studies in Two Bath Chrome Tanning, *by* K. KLAUFER.
17) Studies in Chrome Tanning, *by* E. R. THEIS.
18) Fat Liquor Distribution in Chrome Vegetable Retanned Side Leather, *by* B. ROLL.
19) Aluminum Acetate in Development of Alum Retannage, *by* C. W. BEEBE and J. S. ROGERS.
20) Formate Chemistry—Application to Pickling and Tanning of Chrome Leather, *by* J. W. HARNLY.
21) Use of Polysulfide Liquid Polymers for Impregnation, *by* K. R. CRANKER.

AUDITOR'S REPORT

by ARTHUR W. HOLMES

Certified Public Accountant
University of Cincinnati
Cincinnati 21, Ohio

March 14, 1951.

The American Leather Chemists Association, Inc.,
The University of Cincinnati,
Cincinnati, Ohio.

Gentlemen:

In accordance with the request of Dr. Fred O'Flaherty, Secretary-Treasurer, we have examined the balance sheet of the American Leather Chemists Association, Incorporated, as of December 31, 1950, and the related statements of income and surplus for the year then ended. Our examination was made in accordance with generally accepted auditing standards, and accordingly included such tests of the accounting records and such other auditing procedures as we considered necessary in the circumstances.

The report of the examination is presented herewith, together with the following exhibits:

EXHIBIT I: Balance sheet at December 31, 1950, and comparison with December 31, 1949.

EXHIBIT II: Statement of income for the year ended December 31, 1950 and comparison with the year ended December 31, 1949.

EXHIBIT III: Statement of surplus for the year ended December 31, 1950 and comparison with the year ended December 31, 1949.

The commercial account balance on deposit in the Central Trust Company was confirmed independently and was reconciled with the cash account of the Association.

The United States War Bonds, Series F; the United States Treasury Bonds of the series of 1967–1972; and the United States Treasury Bonds, Series G, were confirmed by Dr. Fred O'Flaherty. They are in the safe deposit box at the Central Trust Company.

Accumulated interest on the Series F War Bonds has been added to the original cost of the bonds. The total accumulated value of the Series F War Bonds at December 31, 1950 is $10,801.00, of which $1,136.00 represents accumulated interest. In the year 1950, all bond investments earned interest of $653.00.

Accounts receivable were not circularized; this procedure was considered unnecessary in view of the small balance of each account, and in view of the fact that of the accounts receivable of $1,743.25 at December 31, 1950, over ninety per cent was collected in January, 1951.

Dues received in advance, totaling $268.10, were verified in detail from the book records. In the same manner, subscriptions received in advance at December 31, 1950, totaling $1,248.89, were verified.

Net profit for the year ended December 31, 1950 amounted to $739.13 compared with $2,379.00 for the year ended December 31, 1949, or a decrease of $1,639.87. The causes of the decreased profit are analyzed in Exhibit II. In the year 1950, revenues increased in the amount of $773.26, while expenses increased $2,413.13. The profit trend over the past several years has been steadily downward.

It is our opinion that the accompanying balance sheet and related statements of income and surplus present fairly the financial position of the American Leather Chemists Association, Incorporated, at December 31, 1950, and the results of its operations for the year then ended, in conformity with generally accepted principles of accounting applied on a basis consistent with that of the preceding year.

Respectfully submitted,

ARTHUR W. HOLMES,

Certified Public Accountant.

EXHIBIT I.

COMPARATIVE BALANCE SHEET
DECEMBER 31, 1950 and DECEMBER 31, 1949

ASSETS

	1950	1949	Increase or *Decrease*
CASH			
Petty Cash on Hand	$ 13.55	$ 8.10	$ 5.45
Cash in Bank	9,637.54	12,650.63	*3,013.09*
RECEIVABLES			
Accrued Interest Receivable on U. S. Treasury Bonds	62.50	62.50	—
Accounts Receivable Advertisers	1,743.25	1,691.00	52.25
INVESTMENTS			
United States War Bonds Series "F" cost $5,920.00 plus accrued interest of $1,136.00 to December 31, 1950	7,056.00	6,888.00	168.00
United States Treasury Bonds—2½% due for redemption in 1972 but redeemable on and after June 15, 1967–Cost	13,000.00	13,000.00	—
United States Treasury Bonds–2½% Series "G" due July of 1958 at Cost	5,000.00	5,000.00	—
United States Treasury Bonds Series "F" cost $3,700.00 plus accrued intereste arned of $45.00 to December 31, 1950. Due in November of 1960 at par	3,745.00	3,710.00	35.00
Total Assets	$40,257.84	$43,010.23	$ *2,752.39*

LIABILITIES

CURRENT LIABILITIES			
Accounts Payable	$ 1,415.92	$ 1,857.94	$ *442.02*
Accrued Withholding Tax Liability	79.20	72.80	6.40
DEFERRED CREDITS TO INCOME			
Advertising Paid in Advance	20.00		20.00
Dues Received in Advance	268.10	2,760.50	*2,492.40*
Subscriptions Received in Advance	1,248.89	1,832.39	*583.50*
Total Liabilities	$ 3,032.11	$ 6,523.63	$ *3,491.52*

NET WORTH

SURPLUS			
Surplus as per Exhibit "C"	$37,225.73	$36,486.60	$ 739.13
Total Net Worth	$37,225.73	$36,486.60	$ 739.13
Total Liabilities and Net Worth	$40,257.84	$43,010.23	$ *2,752.39*

EXHIBIT II

COMPARATIVE STATEMENT OF INCOME & EXPENSE
YEARS ENDING DECEMBER 31, 1950 and DECEMBER 31, 1949

	Years Ended December 31, 1950	1949	Increase *Decrease*
INCOME			
GENERAL			
Dues, (including members' subscriptions to Journal (Net)	$ 8,703.75	$ 8,462.01	$ 241.74
By-Laws & Methods	175.60	310.36	*134.76*
Interest on Government Bonds	653.00	668.00	*15.00*
Membership Booklets (Directory)	460.20	400.80	59.40
TOTALS	$ 9,992.55	$ 9,841.17	$ 151.38
JOURNAL (Exclusive of Members' Subscriptions)			
Advertising	$10,358.90	$10,481.90	$ *123.00*
Subscriptions (Non-Members)	3,775.00	3,352.47	422.53
Journals Bound and Unbound	988.85	661.43	327.42
Reprints	1,360.74	1,396.51	*35.77*
Dues I. S. L. T. C.	614.45	583.75	30.70
TOTALS	$17,097.94	$16,476.06	$ 621.88
TOTAL INCOME	$27,090.49	$26,317.23	$ 773.26
EXPENSES			
GENERAL			
Salary of Secretary	$ 3,433.28	$ 2,599.96	$ 833.32
Office Expenses, Stationery, Postage, Telephone, etc	1,188.84	793.82	395.02
Accounts Receivable Written off	275.00	155.00	120.00
Annual Meeting Expense	5.08	40.04	*34.96*
Auditing	100.00	100.00	—
Association Emblems	286.43	—	286.43
Council Meetings	63.44	137.01	*73.57*
Dues, International Leather	117.60	120.00	*2.40*
Membership Booklets (Directory)	501.25	556.75	*55.50*
President's Letter	73.31	—	73.31
TOTALS	$ 6,044.23	$ 4,502.58	$ 1,541.65
JOURNAL			
Journals	$15,333.34	$15,380.62	$ *47.28*
Editor's Compensation	900.00	900.00	—
Editor's Expense	555.40	427.71	127.69
Insurance Expense (Old Journals)	58.00	58.00	—
Miscellaneous Petty Cash, Postage, etc	33.45	104.81	*71.36*
Registered Copyrights	48.00	48.00	—
Reprints	2,320.15	1,785.15	535.00
Storage	350.00	350.00	—
Exchange on Foreign Checks	2.62	.65	1.97
Translations and Abstracts	273.84	297.82	*23.98*
Committee Work	432.33	82.89	349.44
TOTALS	$20,307.13	$19,435.65	$ 871.48
TOTAL EXPENSE	$26,351.36	$23,938.23	$ 2,413.13

EXHIBIT III

COMPARATIVE STATEMENT OF SURPLUS

	Years Ended December 31 1950	1949	Increase or *Decrease*
Surplus at the beginning of the year	$36,486.60	$34,107.60	$ 2,379.00
Add:			
NET PROFIT			
General (Including members' subscriptions to Journal)	3,948.32	5,338.59	*1,390.27*
Deduct			
NET LOSS			
Journal (Exclusive of members' subscriptions to Journal)	3,209.19	2,959.59	249.60
SURPLUS AT THE END OF THE YEAR	$37,225.73	$36,486.60	$ 739.13

BUDGET FOR 1951

Approved by Council
Feb. 14, 1951

	1950 Proposed	1950 Actual	1951 Proposed
GENERAL ACCOUNT: INCOME			
Dues	$ 5,400.00	$ 8,703.75	$ 8,700.00
Interest on United States Bonds	688.00	653.00	653.00
By-Laws and Methods	100.00	175.00	175.00
Annual Meeting	—	—	—
Directory	400.00	460.20	450.00
	$ 9,588.00	$ 9,992.55	$ 9,978.00
GENERAL ACCOUNT: EXPENSE			
Executive Secretary's Salary	$ 3,200.00	$ 3,433.28	$ 3,500.00
Secretary's Office Expense	500.00	1,188.84	1,000.00
Annual Meeting	200.00	5.00	—
Committee Work	200.00	432.33	500.00
Council Meetings	150.00	63.44	100.00
Auditing	100.00	100.00	100.00
Printing Methods and By-Laws	400.00	—	500.00
Printing Directory	600.00	501.25	500.00
Reserve for Uncollectible Accounts	150.00	275.00	200.00
	$ 5,800.00	$ 5,999.22	$ 6,400.00
Surplus on General Accounts	$ 3,788.00	$ 3,993.33	$ 3,578.00
JOURNAL ACCOUNT: INCOME			
Advertisements	$10,500.00	$10,358.90	$10,000.00
Subscriptions	3,000.00	3,775.00	3,500.00
Journals, Volumes, Reprints, Sold	1,000.00	2,349.59	2,000.00
Dues, S.L.T.C. (Difference)	500.00	614.45	600.00
	$15,000.00	$17,097.94	$16,100.00
JOURNAL ACCOUNT: EXPENSE			
Printing and Publishing	$16,000.00	$15,333.34	$15,000.00
Printing Reprints	2,000.00	2,320.15	2,300.00
Copyright, Insurance, Storage	500.00	456.00	500.00
Abstracts and Translations	300.00	273.84	275.00
Editor's Salary	900.00	900.00	900.00
Office and Misc. Expense (Editor)	500.00	555.40	600.00
	$20,200.00	$19,838.73	$19,575.00
Deficit on Journal Account	$ 5,200.00	$ 2,740.79	$ 3,475.00
Winheim Memorial			$ 100.00
Profit		$ 1,252.54	$ 3.00

MINUTES OF COUNCIL MEETING

AMERICAN LEATHER CHEMISTS ASSOCIATION

February 14, 1951

Hotel Statler
New York, New York

The meeting was called to order at 10:00 A. M. by President Koppenhoefer. The following persons attended—President Elect H. S. Turley, Council Members A. Goetz, R. Ewe, C. Telander, W. Windus, Editor Dean Williams, and Secretary F. O'Flaherty. Visitors were R. Hobbs, John Teas and Fred Thayer.

The minutes of the October 24th meeting were read and given a final approval.

Technical Committee Reports were considered and are covered by the following report of H. G. Turley, Chairman of Technical Committes.

NEW ANALYTICAL TECHNIQUES—DR. SERFASS

No report. Having a meeting this month. Report promised for next Council meeting in June.

PHYSICAL TESTING—MR. MAESER

Writing up methods. Will not start new work until this is done. Maeser now Chairman of the Physical Testing Committees.

ANALYSIS OF MINERAL LEATHERS—DR. SELIGSBERGER

Work on new method for Determination of Combined Sulfates in progress. Samples of chrome leather have been sent out to the Committee, together with the instructions how to proceed. Council discussed this Committee and agreed unanimously for Seligsberger to consider also a method for the Determination of (1) Free Sulfur, (2) a method for the Separation of Pigments, Finishes, etc. Turley will write to Seligsberger.

COMMITTEES ON LEATHER FINISHES

Council unanimously voted to organize a Committee for the Analysis of Leather Finishes. The opinion was unanimous that the Chairman should be from the tanning industry. Suggestions for suitable persons were made to Turley who will try to obtain a Chairman.

PHYSICAL AND MECHANICAL PROPERTIES COMMITTEE

Sub-Committee (b) - Sampling

The Council is anxious to proceed with adoption of approved methods of sampling. Turley was asked to contact Mann of the Quartermaster to find out the present status of his work.

No reports were received from the Chairmen of the other Technical Committees.

H. G. TURLEY.

The following committee matters were considered by Council.

FRENCH HIDE POWDER COMMITTEE. Mr. Sheard had telephoned to President Koppenhoefer and reported that he was acting upon recommendations made in January 1950, and that he had issued new samples of French Hide Powder to be used in vegetable tanning analysis. A report of this work will be made in June 1951.

The question of having some lots of the French type powder made in the United States was discussed. President Koppenhoefer is to consult with Mr. Marshall in reference to this matter.

Council asked Dr. Turley, as Chairman of the Technical Committees, to organize a sub-committee to edit all methods and prepare them for reprinting.

Mr. Thayer presented a report on the plans for the 1951 Annual Meeting at Eastern Point, Groton, Connecticut, June 11, 12, 13. Council expressed satisfaction with the plans.

Dr. Hobbs, Chairman of a sub-committee on By-Laws, presented a number of changes in the present By-Laws. These were approved with some minor changes and are to be re-written and published in the Journal so that they can be voted upon by members at the annual meeting.

Mr. John Teas, Chairman of the Ways and Means Committee, reported on the status of the Association and made a number of recommendations to Council. Council by unanimous vote approved the increase in dues to $12.00 per year and the subscription rate to $15.00. This matter will have to be subject to a membership vote at the next annual meeting. Council has approved the recommendation that a charge of $1.50 per year be made on subscriptions outside the continental limits of the U. S. excepting Canada. Consideration on increase in advertising rates was deferred until the next meeting of Council.

Council approved by unanimous vote that all reprints sold shall be at printing cost plus 25 per cent.

Council approved the 1951 budget as presented by the Ways and Means Committee and the Secretary.

The matter of preparing and publishing a cumulative index was presented by Mr. Williams. The response of members who wanted to purchase copies was so small and the magnitude and cost so great that Council deferred taking any action. President Koppenhoefer is to advise petitioners.

The matter of the A.L.C.A. becoming a member of the American Standards Association was considered and Council was of the opinion that it would not be of any real value to our association. The matter was therefore dropped.

The matter of the 1953 meeting of the International Union of Leather Trade Societies was discussed and Dr. Koppenhoefer is to turn over the correspondence to Dr. Turley who will write for a definite answer.

The following persons were elected to membership: *Active*, Arthur J. Huegel, C. Oncu, Eric Rearden, Jacques Roos, and *Associate*, Charles W. Knisely.

There being no further business the meeting adjourned at 4:00 P. M.

Respectfully submitted,

FRED O'FLAHERTY,

Secretary.

Proposed Program of the London Conference of the International Union of Leather Chemists Societies. September 9 to 14, 1951.

VENUE OF CONFERENCE.

Portland Hall Annexe, Regent Street Polytechnic (Entrance in Little Titchfield Street off Great Portland Street, London, W.1.).

SUNDAY, SEPT. 9th.

Morning . .

Afternoon: Meeting of Executive of the International Union.

Evening, 7–10 p. m. Reception of Delegates and Visitors by the President, J. R. BLOCKEY, Esq., M. Sc., F.R.I.C., at the invitation of the Forestal Land, Timber & Railways Co., Ltd., at the Mayfair Hotel, Piccadilly, London, W. 1.

MONDAY, SEPT. 10th.

Morning 9:30–11 a. m. Meeting of Delegates of International Union.

11 a. m.—Official opening of Conference by the Rt. Hon. The Lord Mayor of London, Alderman Denys Lowson.

Afternoon—This session will be devoted to the reading of scientific papers.

Evening—Meeting of Commissions.

TUESDAY, SEPT. 11th.

Morning—This session will be devoted to scientific papers.

Afternoon—This session will be devoted to scientific papers.

Evening 7–10 p. m. Reception; particulars will be announced later.

WEDNESDAY, SEPT. 12th.

Morning—Visit by coach to the Laboratories of the British Leather Manufacturers Research Association, Milton Park, Egham, Surrey, by invitation of the President and Council of the British Leather Manufacturers Research Association and Dr. Henry Phillips, Director of Research.

Lunch at Great Fosters, Egham, by invitation of Messrs. Barrow, Hepburn & Gale Ltd.

Afternoon, 2 p. m.—Leave by coach for Windsor Castle for a conducted tour of the castle, including State Apartments and St. George's Chapel. Then trip by private launch from Windsor to Marlow, with tea served on board, returning to London by Coach.

THURSDAY, SEPT. 13th.

Morning—Scientific papers.

Afternoon—Opening meeting of Conference to receive reports from Commissions and arrange venue for 1953 Conference.
Closure of Conference.

Evening—Banquet at Park Lane Hotel, London, W. 1., by invitation of the President and Members of the Society of Leather Trades' Chemists.

FRIDAY, SEPT. 14th.

Morning—Annual General Meeting of the Society of Leather Trades' Chemists.

The following Additional Programme has been arranged for the Ladies:

MONDAY, SEPT. 10th.

Morning—It is hoped that the Ladies will be present for the official opening of the Conference and then join the Delegates and other Members at lunch.

Afternoon 2:30 p. m.—Conducted tour of the City of London by Coach, including a visit to St. Paul's Cathedral, and a one-hour conducted tour of the Tower of London.

TUESDAY, SEPT. 11th.

Morning—Visit to the Festival of Britain, South Bank Exhibition, including lunch in the Festival Restaurant.
A visit for a limited number (30) of Ladies to the kitchens and Laboratories of Messrs. J. Lyons & Co., at Cadby Hall has been arranged.

WEDNESDAY, SEPT. 12th.

Ladies are invited to join the party for lunch at Great Fosters, Egham, after a visit yet to be arranged.

NOTE:—Intending visitors to the Conference are again reminded of the desirability of booking their hotel accommodation as soon as possible, because of the great demand in London during the Festival of Britain Celebrations. Arrangements are being made for overseas visitors by the Hon. Secretary, Mr. G. H. W. Humphreys, to whom any communications on the subject should be addressed, c/o Forestal Central Laboratories, Harpenden Rise, Harpenden, Herts, England.

The Determination of Sulfide Ion in Lime and Bate Liquors

ROBERT STUBBINGS

Division of Leather Technology
Institute of Research
Lehigh University
Bethlehem, Pennsylvania

The formation of a bluish-purple color in the reaction of sulfide with sodium nitroprusside has been known for many years and yet few attempts have been made to use this color as a basis for a quantitative measure of sulfide ion. Scagliarini and Pratesi [1] developed an electrometric titration for sulfide ion using Ag_2S and a silve wire stirrer connected to a calomel electrode and titrating with 0.1 N nitroprusside solution. Several investigators including Vinogradov [2] and Morette [3] have suggested nitroprusside as either an external or an internal indicator in the determination of sulfide by iodine titration.

The present investigation deals with the development of a quantitative colorimetric method for the determination of sulfide ion using sodium nitroprusside. Probably the main reason that a colorimetric method has not been recommended is that the nitroprusside color is not stable and so the first necessity was to find a material which would stabilize the color produced.

COLOR STABILIZATION

Increasing the basicity with sodium hydroxide seemed to stabilize the color and also to change the hue from bluish-purple to reddish-purple. Therefore, various alkaline buffers were tried along with sodium hydroxide and the color produced was measured in a Klett-Summerson photoelectric colorimeter using a No. 540 green filter. This choice of filter was made since the color of a blank was yellow and this filter gives a low reading for a yellow solution and a high reading for a red solution.

In Figure 1 (a) the effect of the various alkaline buffers on the color is shown and it is immediately apparent that neither sodium carbonate nor trisodium phosphate can be used while both guanidine and sodium hydroxide offer possibilities. Since the guanidine curve levels off at higher concentrations while the NaOH curve is more sensitive to concentration, it was decided to use the guanidine buffer. This buffer is made up by taking 10 grams of guanidine carbonate, neutralizing with 6 grams of NaOH and making up to 100 ml.

The stability of the color with time is shown in Figure 1 (c) for the various buffers and guanidine shows relatively good stability above about six minutes after the reagents are added. For convenience in routine analysis using this method, it was decided to read the color ten minutes after the reagents were added.

FACTORS INFLUENCING THE SULFIDE-NITROPRUSSIDE COLOR REACTION

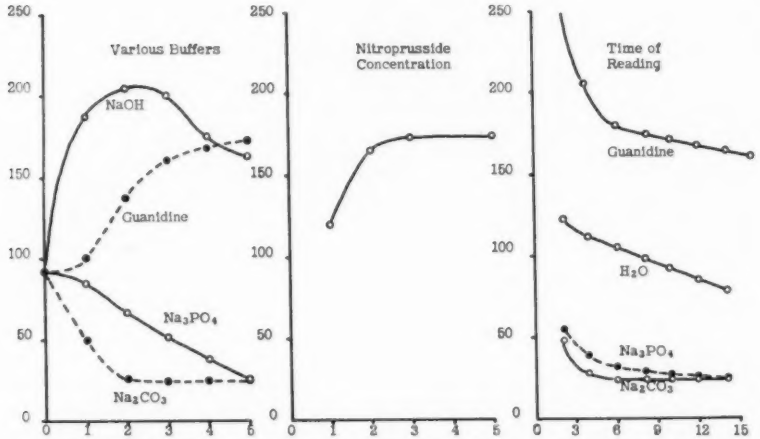


Figure 1

The nitroprusside concentration effect was also studied and the results are shown in Figure 1 (b) for a 1 per cent solution of $Na_2Fe(CN)_5NO.2H_2O$. Since the curve levels off above 3 ml. of nitroprusside added, this quantity of reagent was selected for the method.

Standard Color Curve

The color curve produced with varying known concentrations of sulfide is shown in Figure 2. The points on the curve represent runs with three different batches of both guanidine buffer and nitroprusside solution, and the spread of these points indicates that a standard should be run each time new reagent solutions are prepared. A further precaution to be observed is that the guanidine buffer should be freshly prepared daily since it tends to decompose in the alakaline solution. Figure 2 indicates that this method provides a very sensitive measure of sulfide ion present in solution in concentrations from 0.001 N to 0.006 N.

Analytical Method

The method finally decided upon for the colorimetric analysis of sulfide ion is as follows:

1. Add 5 ml. of sulfide unknown (from .001 N to .006 N) to a 50 ml. volumetric flask.

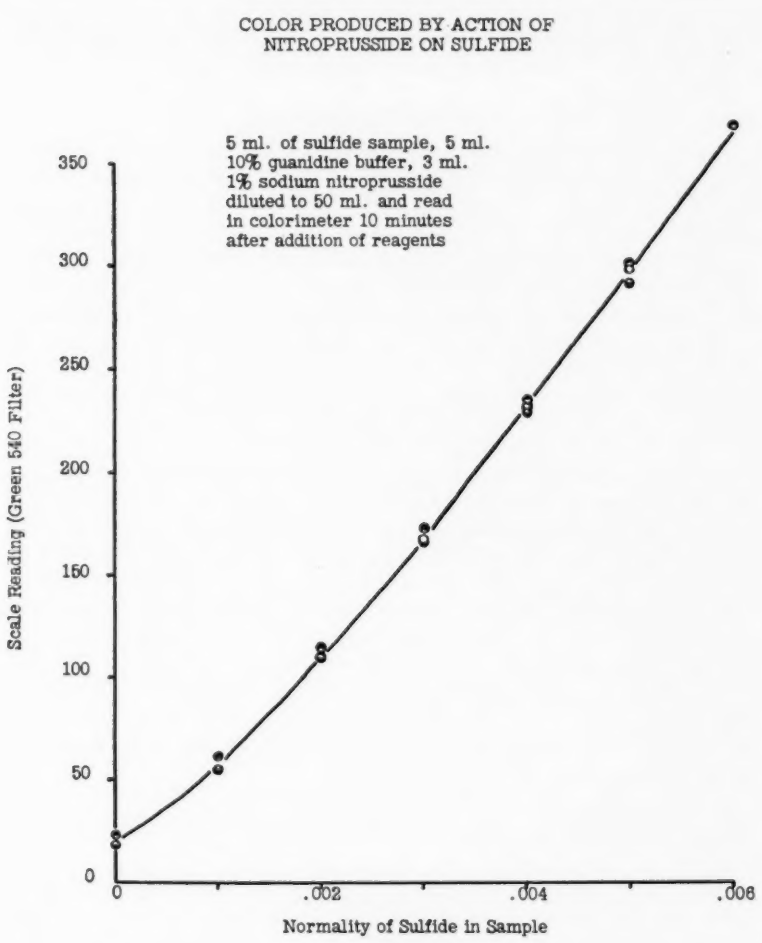


Figure 2

2. Add 5 ml. of 10 per cent guanidine buffer.

3. Thirty seconds later add 3 ml. of 1 per cent nitroprusside solution, and make to volume.

4. Read in colorimeter using Green (No. 540) filter exactly 10 minutes after adding the buffer solution.

5. Compute the sulfide in the unknown from a standard curve made up

with known sulfide concentrations. The sulfide solution should be standardized by any of the regular quantitative methods (iodometric or argentimetric).

Interfering Materials

The method was tested for interference by various substances, and none of the following materials checked showed any appreciable interference: sulfite, cyanide, thiocyanate, thiosulfate, sulfate, sodium hydroxide, glycine, and cystine. It would be expected that materials containing reactive SH groups would be measured although these materials were not investigated. Bermejo and Herrera [4] found that alkyl sulfides from methyl to amyl yielded a color with sodium nitroprusside almost identical with sodium sulfide. Polysulfides would also be expected to react under these conditions as well as cysteine, the reduced form of cystine.

Application of the Method to Lime and Bate Liquors

Since lime liquors measured directly in a colorimeter would give false results because of turbidity, it was necessary to modify the method to avoid this difficulty. Fortunately, this colorimetric method is sufficiently sensitive to require dilution of a lime liquor before measuring anyway and, therefore, two purposes can be accomplished in one step—the dilution of the liquor so that the sulfide concentration falls between .001 N and .006 N and the removal of lime particles from the liquor. Take 20 ml. of the lime slurry in a 100 ml. volumetric flask, add 10 ml. of 1 N NaOH, make to volume, and mix thoroughly. Filter enough of this solution so that 5 ml. may be taken for the sulfide color analysis, and proceed as described under analytical method. The volume of lime slurry taken may have to be varied depending on the amount of sulfide present in any particular lime liquor.

In applying this method to the measurement of sulfide carried over into the wash or bat liquors, the liquor should be filtered and 5 ml. of filtrate analyzed as above.

This method was checked against a gravimetric-iodometric method on eight tannery lime liquors and the results agreed within ± 4 per cent and, therefore, the nitroprusside colorimetric method for sulfide is recommended for rapid tannery control work in the beamhouse.

References

1. Scagliarini, G. and Pratesi, P., *Atti accad. Lincei* **11,** 193, 1930.
2. Vinogradov, A. V. and Dubova, O. A., *Zavodskaya Lab.* **11,** 282, 1945.
3. Morette, A., *Ann. pharm. franc.* **5,** 31, 1947.
4. Bermejo, L. and Herrera, J., *Anales soc. espan. fis. quim.* **31,** 48, 1933.

Received Nov. 8, 1950.

The Improvement of the Tanning Potential of Lignin By Chemical Modifications

By PAUL LIPSITZ* and ROBERT M. LOLLAR

Department of Basic Science in Tanning Research
Tanners' Council Research Laboratory
Cincinnati 21, Ohio

Hydrogen bonding of the vegetable tanning material to the collagen is currently receiving considerable emphasis as a significant mechanism in vegetable tannage. Shuttleworth and Cunningham [25], from a critical review of the literature, concluded that the most logical mechanism was the hydrogen bonding mechanism. Tu and Lollar [30] have recently shown that only those hydroxy derivatives of benzhydrol, benzophenone, di- and tri-phenylmethane, and xanthene which can partake of quinoid resonance are possessed of good tanning properties. From a consideration of the resonance structures involved they concluded that this quinoid resonance enhances hydrogen bonding, thus offering evidence for the hydrogen bonding mechanism in phenolic tannages.

Tu and Lollar [30] point out that in the heterogeneous system existing during tannage (i. e. protein, tannin, non-tannin, and solvents) there are many active centers at which it is possible to speculate that reaction between tannin and collagen occurs. The free amino and carboxyl groups, the guanidyl groups, hydroxy groups and the peptide link itself are all possibilities for reaction loci. Such heterogeneity does not indicate that vegetable tannage occurs by a single mechanism, but the data of Tu and Lollar [30] clearly indicate that, in the case of the phenolic tanning materials studied, hydrogen bonding of the phenolic groups of the tannin to the protein, possibly at the peptide backbone of the collagen, plays a very significant role.

This hydrogen bonding theory of tannage led Lipsitz, Lollar and O'Flaherty [16] to outline a program directed toward a more successful application of lignin derivatives to the tanning industry. Their article pointed out that recent research concerned with the tanning potential of lignin derivatives has given many indications that these materials are a potential source of replacement tannins [12, 14]. They further predicated what chemical modifications the various lignin derivatives required in order to enhance their ability to hydrogen bond with the hide protein and consequently increase their tanning ability.

To investigate this proposal [16] several types of commercially available, low cost, high purity lignin derivatives were subjected to chemical modifications designed to improve their tanning potential by increasing their hydrogen

*The material presented in this paper is taken from the doctorate thesis presented by Paul Lipsitz to the Graduate School of Arts and Sciences of the University of Cincinnati, 1950, in partial fulfillment of the requirements for a Ph. D degree. Present address—Jackson Laboratory, E. I. duPont de Nemours and Company, Wilmington, Delaware.

bonding loci. These derivatives were then given a preliminary evaluation of their tanning potential with calfskin squares. The resultant leather was then examined with regard to "feel", general appearance, and shrinkage temperature.

With the data obtained from the preliminary evaluation, those derivatives offering the greatest promise were selected for further study. This involved the use of a calfskin piece tannage which permitted a more complete determination of the criteria required for leather quality. This was accomplished by making an A.L.C.A. leather analysis, microscopic examination, shrinkage temperature measurement, and a determination of the leathers' resistance to proteolytic enzymes.

In addition to examining the promising derivatives for their tanning potential, fundamental information concerning their chemical composition was obtained by subjecting them to elemental and functional group analyses. The data obtained was useful in correlating their properties with the theory of the tanning mechanism.

Experimental

A. Preparation of the Derivatives

The three types of commercial lignin materials used for the modifications were:

1. A purified alkali hardwood lignin. This material has been described by Plunguian[22] and is available as Meadol.
2. A purified alkali softwood lignin. The product used was Indulin[3].
3. A purified magnesium lignosulfonate obtained from the sulfite process of wood cooking. The prepration of this material has been described by Howard[10] and is available as Marathon Tan A.

A large number of derivatives of these lignins were prepared and subjected to the preliminary evaluation. Many of these were resorcinol condensates with the lignin materials. Several demethylated alkali lignins were also prepared; attempts to demethylate the magnesium lignosulfonate were unsuccessful.

The general procedure for the preparation of the lignin-resorcinol condensates was as follows: Equal weights of the dry lignin material and U.S.P. resorcinol were intimately mixed and placed in a flask fitted with a water cooled reflux condenser and a thermometer. Enough ethyl ether was added to bring the mixture to a pasty mass and then a volume of concentrated hydrochloric acid equal to 10 per cent of the lignin weight was added. The mixture was heated to 120-130°C. and allowed to reflux for 2-3 hours, after which the hot resinous mass was slowly poured into vigorously stirred water. The brown precipitate was allowed to settle, washed repeatedly with water by decantation, filtered and then dried in air. A yield of about 100 per cent based on the lignin taken was usually obtained.

The procedure used for the demethylation of the alkali lignin material was that described by Moore, Wright and Hibbert[18]. It consists of dissolving the lignin in glacial acetic acid, adding 57 per cent hydriodic acid and refluxing the solution several hours in an atmosphere of carbon dioxide. After concentrating the solution, it was added dropwise to a large volume of 0.1 N sodium bisulfite solution which decomposed the excess hydriodic acid and precipitated the demethylated lignin. The insoluble material was separated by centrifugation, washed with water and air dried. If necessary, tar-like impurities can be removed by an ether extraction and if any iodine has combined with the lignin material it can be removed with zinc in glacial acetic acid. A test with silver nitrate on a sodium fusion of the materials before the de-iodination procedure indicated that no iodine was combined and therefore it was unnecessary to subject the demethylated lignins to this process. Yields of 95 per cent based on the dry lignin weights were usually obtained.

Other types of modifications were also made. An ester of 2,4 dihydroxybenzoic acid (beta-resorcylic acid) was prepared with the alkali lignins by a direct esterification in dioxane solution, allowing the vaporized dioxane to carry off the water of reaction. The lignins were chlorinated and the resulting product hydrolyzed with the hope that an increase in phenolic hydroxyl would result. Peniston and McCarthy[21] have claimed the conversion of methoxyl groups in spruce lignin to phenolic hydroxyl groups by a mild alkaline hydrolysis and the lignin derivatives were therefore subjected to that reaction for the desirable conversion. Other methods of demethylation were also employed. Aluminum chloride is known to be a good demethylating agent[9] and so also is 100 per cent phosphoric acid[28] and both of these reagents were used for the lignin modifications. Since lignin is thought to contain a phenyl-propyl-ether type structure[6]. The Claisen Rearrangement[4] with a mixture of glacial acetic and sulfuric acids was employed to increase phenolic hydroxyl groups. Direct condensation of phenol with the alkali soft-wood lignin was also made in the manner described previously for resorcinol.

B. Chemical Analysis of the Derivatives.

In order to have a better knowledge of the composition of the modified lignins they were subjected to elemental and functional group analysis. Since the structure of the lignin employed is unknown and the fundamental unit quite large (about 840) little value could be obtained from the usual carbon-hydrogen analysis. Of much greater interest are such functional groups as methoxyl and hydroxyl and the elements of sulfur and magnesium in the case of the magnesium lignosulfonate derivatives. The methods employed for these analyses follow:

1. Methoxyl—

The standard method (T2M–43) of the Technical Association of the

Pulp and Paper Industry was used [27]. Essentially it is a modified method of Viebock and Schwappach [32].

2. Hydroxyl—
The method used was that described by Siggia [26] and taken from the publication of Ogg, Porter, and Willits [19]. It consists of acetylating the materials with a known amount of acetic anhydride in pyridine and determining the excess by titration with alkali.

3. Sulfur—
The method of Salveson and Hogan [24] was used for sulfur analysis. It is a wet oxidation method (perchloric-nitric acid) with subsequent precipitation of barium sulfate.

4. Magnesium—
Magnesium was determined in the solution obtained by the perchloric-nitric acid oxidation. 8-hydroxyquinoline was used as described by Kolthoff and Sandell [11].

The results of these analyses will be presented later in Tables V, VI, and VII.

C. Preliminary Evaluation of the Tanning Potential.

All of the lignin derivatives prepared were subjected to a preliminary evaluation of their tanning ability by means of tannage of calfskin squares. Since most of the products obtained were insoluble in water, it was necessary, in those instances to employ a solvent system of tannage [23]. Tu and Lollar [30] have shown that methanol is a satisfactory solvent and it was therefore selected for use. The procedure for tannage, essentially that used by Tu and Lollar [30], consisted in immersing several acetone dehydrated calfskin squares (prepared as described by Lipsitz, et al. [13]) in a 20–40 per cent methanol solution of the lignin derivative. After penetration had occurred (16–24 hours), the squares were placed in water for several hours to permit fixation to occur and then the pieces were allowed to air dry in the dark. Where a water soluble material was evaluated, a single bath tannage was conducted in water, the pH of the tanning solution being reduced from 5.0 to 3.0 before removal of the calfskin squares for drying. The dried squares were evaluated for their tanning potential by noting their appearance and feel and measuring their shrinkage temperature [35] in water. The results of this evaluation will be found in Table I.

It will be noted that this table shows that the best leathering characteristics were possessed by the calfskin squares treated with demethylated alkali hardwood lignin, demethylated alkali softwood lignin, the resorcinol condensates of these two lignins, and the resorcinol condensate of magnesium lignosulfonate. The appearance and feel characteristics were the best, and the shrinkage temperature was comparable with that given by the vegetable tannins. Since this increase in shrinkage temperature is not given by the lignins alone, we selected these five materials for further study.

TABLE I

Preliminary Evaluation of the Tanning Potential of Modified Lignins

Lignin Modification	"Feel"	Color	Shrinkage Temperature °C.
Part A—Alkali Hardwood Lignin Used			
Meadol-poly-2,4 Dihydroxy-benzoate	Excellent	Tan	67
Demethylated Meadol	Excellent	Dark Brown	81
Hydrolyzed Chlorinated Meadol*	Fair	Very Dark Brown	62
Alkaline Hydrolysis Product	Good	Brown	66
Resorcinol–Meadol Condensate	Excellent	Tan	80
Part B.—Alkali Softwood Lignin Used			
Indulin-poly-2,4-dihydroxy Benzoate	Very Good	Brown	65
Demethylated Indulin	Excellent	Dark Brown	85
Aluminum Chloride treated Indulin	Fair	Black	62
Phosphoric Acid treated Indulin	Poor	Black	—
Rearrangement of Ether Structure of Phenolic	Good	Brown	64
Hydrolyzed Chlorinated Indulin	Fair	Black	57
Phenol-Indulin Condensate	Good	Brown	70
Resorcinol-Indulin Condensate	Excellent	Tan	79
Alkaline Hydrolysis Product	Fair	Black	61
Part C—Magnesium Lignosulfonate Used			
Lignosulfonate Alkaline Hydrolysis Product*	Fair	Tan	68
Hydriodic Acid Treated Lignosulfonate	Very poor	Black	—
Resorcinol-Lignosulfonate Condensate	Excellent	Tan	81

All tannages of solvent-type except those marked * which are aqueous.

All but two of the materials whose evaluation appear in Table I are too water insoluble for use in present commercial tannery systems. Therefore, it was necessary to study the solubilization of these materials in water. The magnesium lignosulfonate-resorcinol condensate was selected for this study. Sulfonation is a common method to solubilize organic compounds in water, and reaction with bisulfite, where successful, is the simplest commercial method. It was found that the lignosulfonate-resorcinol condensate could be solubilized in water by refluxing it with aqueous sodium metabisulfite.

To determine the optimum concentration of bisulfite required, varying concentrations of bisulfite were refluxed for 24 hours with the lignosulfonate-resorcinol condensate at a solution to solids ratio of 10 to 1, and then cooled. Calfskin squares were then immersed in the resultant solution for several days.

The tanned squares were removed and the shrinkage temperature determined. The experimental data concerning this experiment will be found in Table II. It is evident from the data in Table II that bisulfiting at the 5 per cent level is most effective. Subsequent bisulfiting of the insoluble condensate was carried out at this concentration.

TABLE II

Concentration Studies for
Optimum Bisulfiting Conditions

Magnesium Lignosulfonate-Resorcinol
Condensate taken..... 3.0 g.
Aqueous solution volume .....30.0 ml.
Reflux time.....24.0 hrs.

Concentration of Sodium Bisulfite*	Shrinkage Temperature
1%	74°C.
2	75
3	77
5	80
10	77
15	76
20	75

*Based on lignin derivative.

D. Complete Evaluation of Tanning Potential.

In addition to the five promising derivatives found in Table I, the water soluble product was included in this more complete evaluation. As already indicated, pieces of calfskin (about 3" by 5") were subjected to tannage with the derivatives. The water insoluble materials were employed in a manner identical to that used for the calfskin square tannage, the skin to tannin ratio being 1 to 1, and a solution to skin ratio of 10 to 1. In the case of the water soluble derivative, a single bath tannage at pH 5.0 was used. The skin to tannin ratio was also 1 to 1, but the solution to skin ratio was 20 to 1.

After tannage the pieces were bleached, fatliquored and dried in the manner described in a previous publication [14].

The leathers thus produced were examined with regard to the usual criteria of leather quality. This consisted of:

1. Visual observation for color and handling for determination of general leather character.
2. A modified A.L.C.A. leather analysis. Hide substance, grease and ash were determined in the usual way [35] and water solubles were determined by means of Wilson-Kern washing with water [34].
3. Microscopic examination. Histological examination of cross-sections was made for tannin and fatliquor penetration. In addition, cross-sections were subjected to the ninhydrin test as described by Lipsitz et al [14].
4. A shrinkage temperature determination on the Theis shrinkage meter.
5. A determination of the leathers' resistance to proteolytic attack. The determination, recently developed by Undeutsch and Lollar [31], is conducted in the following manner:

About 0.5 g. of finely ground leather sample is weighed into each of two bottles. Into one bottle 25 ml. of a 0.2 per cent solution of trypsin in 0.1 N sodium bicarbonate is added and the same amount of a similar tryptic enzyme solution, which has been inactivated by boiling, introduced into the second bottle. Both bottles are then agitated at 104°F. for 18 hours. After the digestion has occurred the solutions are made up to 250 ml. in volumetric flasks, filtered with suction, the filtration being aided with "Celite". 50 ml. of the filtrate are then pipetted into tared dishes for solids determination. The difference in solids between the control and experimental sample divided by the weight of dry sample represents the degree of tryptic hydrolysis.

The results of this evaluation together with the data obtained from the other indicated studies will be found in Table III which also lists the properties of a leather made from an unmodified magnesium lignosulfonate. The significance of this data is discussed later.

TABLE III

Complete Evaluation of Leathers Made from Modified Lignins

Tanning Material	Demethylated Meadol	Demethylated Indulin	Resorcinol Meadol Condensate	Resorcinol Indulin Condensate	Resorcinal Magnesium Lignosulfonate Condensate	Bisulfited Resorcinol Magnesium Lignosulfonate	Magnesium Lignosulfonate
Yield % (hide substance basis)	160	152	164	169	157	164	192
Fullness	Poor	Poor	Good	Good	Good	Excellent	Excellent
Firmness	Sl. Stiff	Sl. Stiff	Firm	Firm	Firm	Firm	Firm
Color	Brown Black	Brown Black	Tan	Brown	Brown	Tan	Tan
Shrinkage T. °C.	77	77	83	85	88	79	68
Moisture %	10.1	10.4	9.6	8.8	10.2	10.0	11.1
Total Ash*	0.01	0.02	0.04	0.05	0.11	0.82	0.7
Hide Substance*%	62.4	65.7	61.0	59.2	63.8	61.1	52.1
Chloroform Extract *%	4.7	4.6	7.8	8.3	4.3	3.4	4.4
Wilson-Kern Analysis							
Water Solubles*%	3.0	3.7	9.9	7.3	8.0	23.1	2.3**
Comb. Tannin*%	29.9	26.0	21.3	25.2	23.8	11.6	40.1**
Deg. Tannage*%	48.0	39.5	35.0	42.5	37.4	18.9	76.8**
Tryptic Hydrolysis	22.5	11.1	2.3	8.7	5.4	3.0	43.2
Tannin Penetration	Excellent	Excellent	Excellent	Excellent	Excellent	Light through Center	——
Ninhydrin Reaction	†	†	†	†	†	*	——

*Analysis on dry basis

**Not Wilson-Kern values, but by approved A.L.C.A. methods.

†Leather too dark for absolute detection of blue coloration.

E. Fundamental Studies of the Modified Lignins.

1. Determination of Homo- or Heterogeneity.

Since accurate interpretation of results from functional group analyses depend upon the use of samples representative of a homogeneous entity, it was necessary to determine the homo- or heterogeneity of the lignin derivatives. Therefore, the more promising resorcinol condensates were subjected to ascending, one dimension paper chromatography. Two solvent mixtures for the development of the chromatograms were used: (1) the butyl alcohol-acetic acid-water mixture (4:1:5) used by Partridge [20] and also by White [33] who separated quebracho tannin into many components with this mixture; and (2) the 3:1 mixture of ethyl acetate and methyl alcohol used by Grassman [8] for column chromatograms of vegetable and synthetic tannins. Strips (2.5 by 30 cm.) were cut from Whatman No. 2 paper which was extracted with methanol to remove a fluorescent impurity and spotted 2.5 cm. from one end with 0.5 ml. of solution containing 10-15 micro-grams of solids. The strips were then suspended in the solvent mixtures in closed containers (covered battery jars were employed) and the developing liquid allowed to rise. When the advancing front had travelled two-thirds of the length of the strip, they were removed, air dried and examined under ultraviolet light.

TABLE IV

Paper Chromatography of Modified Lignins

	Developing Mixture					
	Ethyl Acetate-Methanol (3:1)			N-Butyl Alcohol-Acetic Acid-Water (4:1:5)		
Lignin Derivative	Rf.	Visible Color	Color under Ultraviolet	Rf.	Visible Color	Color under Ultraviolet
Resorcinol-Indulin	1.0	Orange	Yellow	1.0	Orange	Yellow
Resorcinol-Meadol	1.0	Orange	Blue-White	1.0	Orange	Yellow
Resorcinol-Magnesium Lignosulfonate	1.0	Orange	Blue-White	1.0	Colorless	Blue-White
				0.98	Orange	Yellow
Fraction 106-T	1.0	Orange	Blue-White	1.0	Orange	Yellow
Fraction 106-N-T	1.0	Orange	Blue-White	1.0	Orange	Yellow

Table IV indicates the results obtained. In every case except the resorcinol-magnesium-lignosulfonate condensate, a single band resulted as is evident from the single Rf value (rate of migration of the spot on the paper) obtained. With the resorcinol-magnesium-lignosulfonate, however, the butyl alcohol-acetic acid-water mixture gave two Rf values, differing only slightly, but significantly. These two bands indicate the presence of at least a two component system.

2. Separation of the Components in the Magnesium Ligno-sulfonate Resorcinol Condensate.

Preliminary experiments with a chromatographic column of calcium carbonate indicated also that two substances were present. Both materials were methanol soluble, but one fluoresced with a yellow color when its methanol solution was placed under ultraviolet light while the other substance gave a blue-white fluorescence. Neither calcium carbonate, alumina, nor hide powder produced a completely satisfactory chromatographic column, but the hide powder column indicated that the use of hide powder in a batch process might preferentially adsorb one of the components. It should then be possible to leach off the fraction adsorbed with a 50-50 water-acetone mixture, which Merrill[17] has shown to be very effective in removing many tannins from hide powder. Details of the method employed follow:

312 g. of a grease extracted, methanol washed hide powder was placed in water and allowed to stand for thirty minutes. After filtering with suction the hide powder was added to 5 liters of methanol containing 18.7 g. of the magnesium lignosulfonate resorcinol condensate and the mixture was stirred vigorously for one hour. The tanned hide powder was washed once with methanol and allowed to air dry overnight. The filtrates were combined for further treatment.

The air dry, tanned hide powder was then extracted by repeated shakings with four 2 liter portions of a 50-50 acetone-water mixture. Although all of the material was not removed, the fourth extraction recovered very little material. These extracts were then concentrated to yield 6.4 g. of material (designated 106-T) which represents 34.2 per cent of the amount taken (18.7 g.). When dissolved in methanol the substance exhibits a blue-white fluorescence under ultraviolet light.

The filtrate and washing which contained the material not adsorbed by the hide powder were combined and concentrated to yield 3.9 g. of solids which is 20.9 per cent of the total amount taken (18.7 g.). This material when dissolved in methanol produced a yellow fluorescence under the ultraviolet lamp.

Each of these fractions were again chromatographed and in each case a single band was obtained. Thus it appears that a separation was achieved.

Discussion

Since the structure of lignin is not known with precision, we can not interpret the course of the reactions secured exactly. Therefore, we were unable to examine the reasons why many of the compounds prepared were not possessed of improved tanning character. We choose to place our emphasis on an investigation of the reasons why some of the compounds did possess

better tanning properties than the unmodified lignin. This investigation suggests a definite correlation between the increase in phenolic hydroxylation of the lignin derivatives and the improved tanning ability, which confirms the premise on which this research was undertaken.

Table III indicates the data obtained from the complete evaluation of the six best modified lignins. It is evident that the demethylated lignins produced leather with a poor general appearance, but which did have an elevated shrinkage temperature and was considerably more resistant to tryptic attack than the leather made from the unmodified lignosulfonate. The leathers made from the resorcinol condensate derivatives are, in general, excellent in regard to visual observation and "feel" characteristics. They, too, have an elevated shrinkage temperature and are quite resistant to tryptic attack, having the same range of hydrolysis as vegetable tanned leathers [3].

The yield obtained and the degree of tannage was in all cases somewhat low, reflecting the high hide substance value. Unfortunately the results of ninhydrin reaction [4] are not as definite as one would like. Only in the case of the bisulfited magnesium lignosulfonate resorcinol condensate was there a decided blue coloration. In the other instances, the leather cross-sections were so dark that no blue coloration could be seen. There was however a decided further darkening when these cross-sections were treated with the ninhydrin reagent which would seem to indicate a positive reaction. The interpretation of the positive reaction is that inactivation of the free amino groups of the hide protein has not occurred and therefore the tanning mechanism does not involve reaction at these loci. The significant data obtained in the test is that the bisulfited resorcinol condensate produced a positive reaction in contrast to the unmodified lignosulfonate tanned leather. Further, the leather made from the new derivative has met the criteria established for leather quality which is not met by the unmodified lignosulfonate. Since the bisulfited resorcinol condensate is the result of increasing the hydrogen bonding loci of the magnesium lignosulfonate it follows that the basic contention of the tanning mechanism (i.e. that leathering properties result from hydrogen bonding) is of considerable significance.

Tables V, VI, and VII indicate the analytical data obtained from the modified lignin derivatives. The analysis of the demethylated lignin derivatives (Tables V and VI) indicates that the hydriodic acid treatment reduced the methoxy content about 12 per cent. Although only a small increase in hydroxy content is evident it must be remembered that treatment with hydriodic acid destroys the aliphatic hydroxyl groups and the per cent hydroxyl after demethylation represents phenolic hydroxyl. In addition to the destruction of the aliphatic hydroxyl groups, considerable degradation of the lignin structure probably occurred since the lignin structure is reported to contain ether linkages in its fundamental unit [6]. This breakdown is reflected in the rather poor leather quality obtained from tannage with these

materials. Thus, the only conclusion warranted is that the phenolic hydroxyl content has been considerably increased with a subsequent increase in shrinkage temperature and resistance to tryptic attack of leather made from such modified lignins.

TABLE V

Analytical Data on Products Derived from Alkali Hardwood Lignin (Meadol)

(All data on dry basis)

	Meadol	Resorcinol Meadol	Demethylated Meadol
Methoxy (% OCH_3)	21.6	14.5	9.2
Hydroxy (% OH)	9.9*	17.0	14.7
Number Methoxy Groups per 860 Unit Weight	6.*	6.	
Calculated Unit Weight Based on 6 Methoxy	860.	1285.	
Number of Hydroxy Groups	5.**	13.**	
Number of Hydroxy Groups Added		8.	
Calculated Unit Weight from 4 resorcinol molecules added per 860 unit weight		1300.	

*Calculated from the literature (13).
**Calculated from the analysis.

TABLE VI

Analytical Data on Products Derived from Alkali Softwood Lignin (Indulin)

(All data on dry basis)

	Indulin	Resorcinol Indulin	Demethylated Indulin
% Methoxy	13.9	8.8	1.1
% Hydroxy	14.5	16.8	15.8
No. methoxy groups per 840 unit*	4.	4.	
Calc. mol. wt. on 4 methoxy	840.	1410.	
No. of hydroxy groups**	8.	14.	
No. hydroxy groups added		6.	
Calc. mol. wt. based on addition of 5 resorcinol molecules per 4 methoxyl		1390.	

*Calculated on basis of analysis, which is in agreement with Manufacturers' Bulletin (3).
**Calculated from analysis.

The analysis of the alkali hardwood lignin resorcinol condensate is compared with that of the unmodified lignin in Table V. If one assumes that the literature is correct and that this type of lignin has a unit weight of 860 and that this unit contains 6 methyoxy groups [12], some interesting calculations

TABLE VII

Analysis of Magnesium Lignosulfonate Derivatives

Derivative	Per cent Mg.	Per cent S	Per cent OCH_3	Per cent OH	OH/OCH_3
Magnesium Lignosulfonate	2.5	6.5	10.0	11.0	——
Magnesium Lignosulfonate Resorcinol Condensate	0.22	2.0	7.9	16.6	3.8:1
Bisulfited Magnesium Lignosulfonate Resorcinol Condensate	——	4.2	7.2	16.9	4.3:1
Fraction 106-T*	——	1.3	7.4	16.1	——
Fraction 106-N-T**	——	0.94	8.1	18.8	——

*A dilute methanol solution of this fraction gave us a blue white fluorescence when placed under ultraviolet light.

**A dilute methanol solution of this fraction produced a yellow fluorescence when placed under ultraviolet light.

can be made. It follows from the nature of the modification that the number of methoxy groups was not affected and therefore the unit weight of the resorcinol condensate can be calculated thus:

$$\frac{\text{No. of } OCH_3\ (6) \times \text{Mol. Wt. } OCH_3\ (31) \times 100}{\text{Unit Weight}} = \text{per cent methoxy (14.6)}$$

$$\therefore \text{ Unit weight} = 1285$$

From this unit weight, the number of hydroxyl groups present in the derivative can be obtained.

$$\frac{\text{No. of OH groups} \times \text{Mol. Wt. OH (17)} \times 100}{1285} = \text{per cent OH (17.0)}$$

$$\therefore \text{ No. of OH groups} = 12.9 \text{ or } 13$$

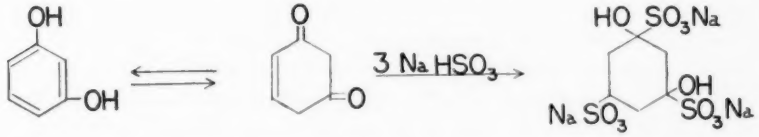
Therefore since five hydroxyl groups are present in the unmodified lignin [13], eight hydroxyl groups must have been added by the reaction.

As a further check on this conclusion it is found that the unit weight of the resorcinol condensate is 1300 if four resorcinol molecules have been added per 860 unit : 860 + (4 x 110) = 1300. This is a good check on the value calculated from the analytical data. Thus it appears that the reaction between this alkali hardwood lignin and resorcinol involves the addition of four resorcinol molecules per lignin unit of 860 and the data further suggests that the reaction does not involve hydroxyl groups.

Similar reasoning from the analytical data for the alkali softwood lignin resorcinol condensate (Table VI) indicates that six hydroxy groups have been added per lignin unit of 840. The unit weight calculated from the analytical data is 1410 which is in agreement with the value obtained (1390) on the assumption that five resorcinol molecules combine with the lignin. Thus it would appear that the reaction between the alkali softood lignin and resorcinol involves the addition of five resorcinol molecules per lignin unit of 840 and that four hydroxyl groups are involved.

The interpretation of the analytical data obtained in the case of the magnesium lignosulfonate resorcinol condensate (Table VII) is limited because the material is not homogeneous. The two fractions that have been obtained are decidedly different, but no other conclusions about them can be made.

Of considerable interest however are the hydroxyl to methoxyl ratios of the water insoluble and bisulfited derivatives. Again making the logical assumption that the methoxyl content should not change with bisulfiting, it is at once apparent from the ratios that the hydroxyl groups were not affected by the sulfiting reaction since, if they had been, a decrease in the ratio would have been noted. An argument against this conclusion might be made on the basis of the data of Bucherer [2] and Fuchs and Elsner [7] who found that resorcinol can be sulfonated with bisulfite and postulated that the reaction would involve the tautomeric enol form as follows:



It is true that such a reaction would involve no change in the hydroxyl to methoxyl ratio, but the resulting compound would not be a tanning material because the phenolic character of the hydroxyl groups no longer exists. Since the bisulfited derivative has good tanning ability, the original deduction that the hydroxyl groups are not involved would appear to hold.

It is evident that the data presented in this paper support the view that this program for the improvement of the tanning potential of lignin derivatives is well founded. It is obvious, however, that additional research must be carried out to make any process toward this goal economically sound. The chemical modifications of the type indicated would not seem to lend themselves to low cost processes, but there are several conceivable approaches to low cost modifications. The demethylated lignins which were prepared in this work suggest themselves as a source of phenolic substances for condensation with the unmodified lignins. The use of a continuous process for demethylation with hydriodic acid would no doubt permit recovery of the liberated methyl iodide as a valuable by-product and thus reduce the modification cost to a reasonable figure. Another possible means of demethylation that could probably be made economically feasible is by the use of microorganisms trained to metabolize aromatic methoxyl groups leaving phenolic hydroxyl as the desired product. It is also evident that such lignin modifications are well suited not only to the leather industry, but to many other fields of the chemical industry.

It is interesting to note in Table I that the alkali lignin-poly-2,4 dihydroxy benzoates produced leather samples that had good appearance, with no in-

crease in shrinkage temperature. At first this might appear contradictory to the hydrogen bonding theory of the tanning mechanism since phenolic hydroxyl groups have been added to the lignin. Tu and Lollar [30] have shown that tanning properties cannot be expected from meta substituted phenolic hydroxyl groups and it follows from a consideration of resonance structures that they cannot be expected from aromatic hydroxy carboxylic esters. The carboxyl resonance of the ester linkage creates greater stability to the Kekule' resonance of the aromatic ring and therefore limits to a large degree the quinoid resonance in the resorcinol ring. Therefore the hydrogen atoms of the phenolic hydroxyl groups have little tendency to hydrogen bond. On the other hand, a consideration of the resonance structures of ortho and para dihydroxy diphenyl and polyphenyl sulfones indicates that they should be tanning materials and the recent reports [1] on sulfone type tannins corroborates this interpretation. In the diphenyl sulfone type of structure the quinoid resonance is enhanced by the various structures of similar energy that can be written for it and this therefore permits the hydrogen of the phenolic hydroxyl groups to take part in hydrogen bonding.

The above interpretation might be questioned on the basis that hydrolyzable tannins are aromatic hydroxy carboxylic esters and that they do convert hide protein into leather. But the additional fact remains that Lipsitz et al. [15] have recently shown that chestnut tannin, a representative of the hydrolyzable tannins, does not make a leather that resists proteolytic attack. This raises the interesting question as to whether or not other tannins in this class exhibit the same characteristics. Additional evidence that leather made from hydrolyzable tannins are susceptible to enzymatic attack may be found in the work of Thomas and Seymour-Jones [29] who noted that hide powder treated with gallotannin, another hydrolyzable tannin, was considerably attacked by trypsin. It is true that this class of tannins produces leather with an elevated shrinkage temperature (although chestnut tanned leather has, in general, a lower shrinkage temperature than leather made from the condensed tannin types; viz. quebracho and wattle) and an explanation for the tanning ability of chestnut can be found in the querciten part of the chestnut tannin which structure is postulated by Flinn [5]. This polyhydroxyflavanone structure contains phenolic hydroxy groups which can take part in quinoid resonance and are therefore loci of hydrogen bonding. Thus the hydrogen bond theory adequately accounts for the facts observed.

A mild alkaline hydrolysis of the lignins might be expected to produce suitable tanning materials since as already noted, Peniston and McCarthy [21] have shown that such treatment increases the phenolic hydroxyl content and decreases the sulfonic acid character of the lignin. Unfortunately, this treatment also results in considerable breakdown of the lignin material. It is well known that particle size of the tanning material is an important factor in affecting a tannage. Very probably, the failure to obtain a satisfactory

tanning material from an alkaline hydrolysis modification is the result of such extreme lignin breakdown.

Summary

The suggestion that modified lignin derivatives are a potential source of domestic tanning materials is predicated upon the hydrogen bond theory of vegetable tannage. Three types of commercially available lignins have been subjected to chemical modifications designed to increase their hydrogen bonding ability with a consequent increase in tanning potential. The derivatives thus obtained were given a preliminary evaluation by means of a calfskin square solvent tannage and the most promising derivatives selected for further study. In addition to the promising water insoluble derivatives which included

a. A demethylated alkali hardwood lignin,

b. A demethylated alkali softwood lignin,

c. A condensate of resorcinol with an alkali hardwood lignin,

d. A condensate of resorcinol with an alkali softwood lignin,

e. A condensate of resorcinol with a magnesium lignosulfonate, a water soluble derivative was also prepared by bisulfiting the resorcinol magnesium lignosulfonate condensate. These six lignin derivatives were used to tan pieces of calfskin and the resulting leathers given a complete evaluation in regard to shrinkage temperature, general leather "feel" and appearance, chemical and microscopic analysis, and resistance to proteolytic enzymes.

In addition to the above evaluation, fundamental information concerning the derivatives themselves was obtained. This consisted of elemental and functional group analysis. A study was also made of the homo- or heterogeneity of the compounds by paper chromatography and where a separation of the components was made, each fraction was subjected to chemical analysis.

The data obtained in this investigation permit the following conclusions to be made:

1. As predicated, increasing the phenolic hydroxyl content of lignin derivatives converts them to improved tanning materials. This is additional evidence for the significance of hydrogen bonding in the tanning mechanism.

2. Leather produced from such modified lignins have leather character ,not obtainable from the unmodified lignosulfonate tannage, i. e. increased shrinkage temperature, and resistance to enzymatic hydrolysis.

3. Lignin resorcinol condensates are better tanning materials than demethylated lignins.

4. A bisulfited magnesium lignosulfonate resorcinol condensate is an excellent water soluble tanning material.

5. The reaction between sodium bisulfite and the magnesium lignosulfonate resorcinol condensate does not involve hydroxy groups.

6. The reaction between an alkali hardwood lignin and resorcinol results in the introduction of four resorcinol molecules per lignin unit and the data suggest that the hydroxyl groups are not involved.

7. The reaction between an alkali softwood lignin and resorcinol results in the addition of five resorcinol molecules per lignin unit and the data suggest that four hydroxyl groups are involved.

8. The magnesium lignosulfonate resorcinol condensate is a mixture of two components. Preferential adsorption of one fraction on hide powder permits a separation yielding two distinct fractions.

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The Determination of Nitrogen in Leather by the Kjeldahl Method*

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I. INTRODUCTION

When different laboratories analyze leather for percentage of hide substance, the variation of results between laboratories may often be as high as two percent. This was shown by a series of cooperative check analyses made by seven laboratories represented in the American Leather Chemists Association (ALCA), using the Official method of the Association. Such a variation, serious enough in itself, leads to a corresponding error in the value for the combined tannin, which is calculated by subtracting the sum of the hide substance and certain other constituents from 100 per cent, and is multiplied in computing the degree of tannage, obtained by dividing the combined tannin by the hide substance. Thus differences between laboratories of five per cent in the result for degree of tannage are not uncommon.

Since the hide substance is itself calculated by multiplying the percentage of nitrogen in the leather by the factor 5.62, any errors in the original analysis are greatly magnified by the time the value for the degree of tannage is reached, and it becomes necessary to reduce errors in the nitrogen determination

*Most of these data and conclusions were presented at the Forty-fifth Annual Meeting of the American Leather Chemists Association, Spring Lake, N. J., June 22, 1949.

as much as possible to get reproducible values for degree of tannage. The check analyses made by the cooperating laboratories showed that each laboratory was generally able to duplicate its own results satisfactorily, that is, to within 0.5 per cent at most, but that the major differences lay between laboratories. This circumstance would be of little concern in process control analysis in a tannery, but it is of great importance in furnishing leather of a specified degree of tannage to a large consumer such as an agency of the Federal Government, and makes uncertain the evaluation of research on new tanning materials or processes reported by other laboratories.

The agreement within laboratories and differences between them suggested that variations in procedure permitted by the ALCA method or variations from the specified procedure, generally assumed to be negligible, might be responsible for the discordant results. At the request of the Council of the ALCA, the National Bureau of Standards undertook the investigation reported in this paper.

The Kjeldahl method for the determination of nitrogen has been one of the most widely studied of all analytical procedures. For an introduction to the literature on this subject, the reader is referred to Seebold's review [1]. Of the three main steps in the method, digestion, distillation, and titration, only the the first presents important problems that are peculiar to leather. Attention was therefore directed largely to this step, and choice of catalyst, temperature and time of digestion, composition of digestion mixture, and weight of sample were studied.

II. Digestion

In spite of much published research on the merits of copper, selenium, and mercury catalysts for accelerating the digestion with sulfuric acid, it is not clear which is preferable for leather, or how safely one can assume that they will yield equal results. Other factors, such as temperature and time of digestion, and weight of specimen, play an important part, and may produce a differential response with the same catalyst. These have all been considered in this work.

1. *Apparatus and General Procedure*

All digestions were carried out in 800-ml Kjeldahl flasks, placed in a rack so that the necks of the flasks were inclined a little more than 45° from the vertical, and with the mouths of the flasks inserted in a duct with a forced draft to carry away fumes. The flasks were heated by a gas flame. In order to measure temperature of the digestion mixtures, some flasks were provided with theremometer wells extending to about 3 mm from the bottom of the flask. A small amount of Wood's metal in the well served as a contact liquid for the thermometer.

When mercuric oxide was used as the catalyst, 25 ml of an 8 per cent solution of sodium thiosulfate penta-hydrate was used to precipitate the mercury

before distillation. Distillation was conducted over a gas flame, with boric acid solution as absorbent for the distillate. The absorbent was 4 per cent boric acid in water, to which was added a mixed indicator of methyl red and methylene blue in the ratio of 6 ml of methyl red solution and 4 ml of methylene blue solution per liter of boric acid solution. Each indicator solution was of 0.1 per cent concentration, in 95 per cent ethanol. In general, 50 ml of this boric acid indicator solution was used as the absorbent. When a 1.5-gram specimen of leather was used, this was increased to 75 ml.

Titration was effected with dilute sulfuric acid, standardized against sodium hydroxide solution, which in turn was standardized against a National Bureau of Standards standard sample of acid potassium phthalate. In all other respects the Official ALCA method was followed, except as will be described below for specific experiments.

2. *Samples of Leather Used*

For the studies of the digestion procedure, three samples of leather, chosen so as to offer definite contrasts in tannage and grease content, were used. The samples were ground in a Wiley mill to pass a 4-mm screen, mixed thoroughly, then passed through the mill a second time and again mixed. The samples were then conditioned for a week in air at 73°F and 50 per cent relative humidity, after which they were kept in tightly screw-capped glass bottles. In the table below are given some pertinent data on these samples.

Identification Symbol	Type of Leather	Grease per cent	Moisture per cent	Ash per cent
I	Chrome-tanned side upper	31.4	11.5	3.42
II	Vegetable, heavy	3.5	12.7	0.91
II	Sample I, degreased	——	15.1	5.02

3. *Temperatures of Boiling Mixtures of Sulfuric Acid with Sodium Sulfate or with Potassium Sulfate*

Variation in the temperature of the digestion mixture has been suggested as a possible souce of discrepancies between results obtained by different laboratories in determining the hide substance in leather. The temperature of boiling mixtures of sulfuric acid with sodium sulfate or with potassium sulfate was therefore measured. In a series of determinations, 4, 8, 12, 16, 20, 24, and 28 grams, respectively, of each of these two sulfates, were added to 20-ml portions of concentrated sulfuric acid in Kjeldahl flasks equipped with thermometer wells. The mixtures were boiled for 30 minutes, taking care to keep the condensation line within the neck of the flask, and the temperatures were then observed. Duplicate determinations in different flasks and over different burners always agreed within 2°C. Addition of catalysts in the amounts used

in the Kjeldahl digestions had no measurable effect. Results are given in Table 1.

TABLE I

Temperatures of boiling mixtures of sulfuric acid with potassium or sodium sulfate.

Sulfate added to 20 ml H_2SO_4	Temperature of K_2SO_4 mixture		Temperature of Na_2SO_4 mixture	
	observed	calculated*	observed	calculated*
grams	°C	°C	°C	°C
0	320	321	320	321
4	327	329	327	328
8	334	336	334	334
12	342	—	340	—
16	350	—	345	—
20	359	—	350	—
24	365	—	356	—
28	370	—	361	—

*Calculated from data given in the International Critical Tables (2)

For the lowest concentrations, comparable values calculated from data in the International Critical Tables [2] are also given. Similar calculations for higher concentrations would have involved excessive extrapolation from the data in the Tables.

From these data it appears that the temperature of the digestion mixture would be changed only a degree or two by a variation of as much as one gram in the amount of sodium or potassium sulfate added to the sulfuric acid, and that, within the range of concentration ordinarily employed, it is immaterial so far as the temperature of the digestion is concerned, whether sodium or potassium sulfate is used.

The use of the higher concentrations of salt may lead to one inconvenience in practice, as the digestion mixture tends to solidify when cooled, thus requring more time to dissolve the mixture in water when it is diluted preparatory to distillation. A quantity of 8 grams of the salt seems to be adequate and practicable.

4. *Variations in Conditions of Digestion*

Important effects of variations in the conditions of digestion are the influence on the quantitative conversion of nitrogen from the specimen to ammonium sulfate and the acceleration of the digestion. The choice of catalyst, the use of sodium sulfate or potassium sulfate, the period of time during which the mixture is heated, and the relative size of the specimen may all influence these effects. The three catalysts that have been found most efficient and are most widely used are copper sulfate ($CuSO_4.5H_2O$), selenium metal,

and mercuric oxide. These catalysts were therefore used in the study reported here.

Three series of determinations were made on the leathers to permit the following observations to be made on the results: (1) a comparison of the effect of sodium sulfate in the digestion mixture with that of potassium sulfate; (2) a comparison of the effects of the three catalysts, with different periods of digestion and weights of specimens, the digestion mixture being the same in each case; and (3) a comparison of the catalysts using different digestion mixtures, the period of digestion and the weight of specimen being the same in each case.

The experiments were designed so that suitable statistical analysis could be applied to the results. All determinations were made in duplicate. In no case did duplicate determinations under optimum conditions differ by more than 0.65 per cent and the mean difference of 54 duplicates was 0.13 per cent. The results are given in per cent hide substance.

(1) Comparison of sodium sulfate with potassium sulfate

In order to compare the relative effect of sodium sulfate and potassium sulfate in the digestion mixtures, a series of determinations was made in which, for each salt, the hide substance in each of the three leathers was analyzed using each of the three catalysts and each of three digestion mixtures. For sodium sulfate, the three mixtures contained 3, 6, and 12 grams, respectively, of sodium sulfate; and for potassium sulfate, 4, 8, and 16 grams. The ratio of 3 grams to 4 grams for sodium to potassium sulfate represents approximately molar equivalents [3]. Twenty ml of sulfuric acid were used in each digestion.

The weight of the leather specimen was 0.5 gram for each determination. The period of digestion was that which would give maximum recovery of nitrogen, as indicated by preliminary experiments, and was two hours for the copper catalyst, one hour for the mercury and selenium catalysts. The concentrations of catalysts were: for the copper sulfate, 0.8 gram per determination; for the selenium, 1.0 gram per 100 grams of sodium sulfate or per 133 grams of potassium sulfate; and for the mercuric oxide, 7 grams per 100 grams of sodium sulfate or per 133 grams of potassium sulfate. The selenium and mercury catalysts were thoroughly mixed with the sulfates before addition; the copper sulfate crystals were added directly to the Kjeldahl flasks.

An inspection of the results, shown in Table 2, indicates that there was no significant difference between the values obtained with sodium sulfate and those obtained with potassium sulfate. This conclusion was verified by a statistical analysis of variance. The results show that the digestion temperatures, measured for leather I only, are approximately those to be expected from the data in section II, 3, above. Clearing times (time required for disappearace of the dark color of the digestion mixture) are also about the same for the two salts. In order to save time in the digestion, it appears that at least 6 grams of sodium sulfate, or 8 grams of potassium sulfate should be

TABLE 2

Comparison of effect of sodium sulfate in digestion mixtures with that of potassium sulfate.

Sodium sulfate*

Catalyst	$CuSO_4.5\ H_2O$				Se				HgO			
Leather	Na_2SO_4 g	Clearing time min.	Temp. °C	Hide Sub.** per cent	Na_2SO_4 g	Clearing time min.	Temp. °C.	Hide Sub.** per cent	Na_2SO_4 g	Clearing time min.	Temp. °C.	Hide Sub.** per cent
I	3	53	325	46.35	6	17	333	47.65	12	12	342	47.75
II	6	21	—	43.70	12	10	—	43.85	3	25	—	43.95
III	12	12	—	70.85	3	18	—	70.20	6	14	—	70.85

Potassium sulfate*

Catalyst	$CuSO_4.5H_2O$				Se				HgO			
Leather	K_2SO_4 g	Clearing time min.	Temp. °C	Hide Sub.** per cent	K_2SO_4 g	Clearing time min.	Temp. °C.	Hide Sub.** per cent	K_2SO_4 g	Clearing time min.	Tiemp. °C	Hide Sub.** per cent
I	4	52	326	46.60	8	17	334	47.55	16	11	353	47.95
II	8	15	—	43.80	16	13	—	43.60	4	24	—	43.85
III	16	11	—	70.80	4	20	—	70.15	8	13	—	71.05

*20 ml H_2SO_4 used in each digestion.

**Each value is the mean of two determinations.

used. The mercury catalyst seems to yield higher results than either of the other catalysts.

(2) Comparison of three catalysts, using different periods of digestion and weights of specimens

The difference in the effects of the catalysts, suggested by the results in the section immediately above, was investigated further by an experiment in which the same digestion mixture was used for all three catalysts, while the weights of the leather specimens and the period of digestion were varied.

Three weights of specimens were used, 0.5, 1.0, and 1.5 grams. For the first two, the digestion mixture consisted of 8 grams of potassium sulfate with 20 ml of sulfuric acid. When a 1.5 gram specimen was used, it was necessary to use 10 grams of the salt with 25 ml of the acid, in order to get satisfactory wetting of the leather.

The digestion periods with $CuSO_4.5H_2O$ as catalyst were 1.5, 2.0, and 2.5 hours; with selenium and with mercuric oxide as catalyst, the periods were 0.5, 1.0, and 1.5 hours. The comparison of the catalysts was desired when the optimum digestion time for each was used, and the additional hour for copper sulfate was found to be needed to obtain values for nitrogen close to the maximum for each leather. The concentrations of catalysts were: copper sulfate, 0.8 gram per determination; selenium, 2.4 per cent of the potassium sulfate-selenium mixture; and mercuric oxide, 6.5 per cent of the potassium sulfate - mercuric oxide mixture.

The results are shown in Table 3. The clearing times indicate the respective efficiencies of the three catalysts in accelerating the digestion, although they are not reliable in judging the "after boil" required for complete digestion. As copper sulfate does not give maximum values until at least 2 hours of digestion, the ALCA specification of 10 minutes digestion after clearing is not nearly enough. An "after boil" of half an hour seems necessary even for the selenium and mercuric oxide catalysts.

Digestion temperature rose slowly for the first hour, probably because of evaporation of water, reaching the following values for the different weights of specimen: for 0.5 gram, 336°C; for 1.0 gram, 340°C; and for 1.5 grams, 342°C. The increase in temperature with increasing weight of specimen might be expected from the fact that more acid is decomposed in digesting a larger sample, thereby increasing the ratio of salt to acid.

Mercuric oxide generally gives the highest values, though these are in fair agreement with the values obtained with copper sulfate provided optimum periods of digestion are used. Similar results have been reported by Frey and Jenkins[4]. The tendency to obtain low values with selenium is noticeable., this tendency being increased by heating longer than the optimum time, or by using a larger specimen.

An analysis of the variance of the precision of the duplicate values whose averages are given in Table 3 showed that significantly better precision was

TABLE 3

Effect of catalysts on determination of hide substance in leathers, with different weights of specimen and different periods of digestion.

Catalyst		$CuSO_4.5H_2O$				Se				HgO			
Leather	Wt. of specimen	Digestion period (hr.) 1.5	2.0	2.5	Clearing time	Digestion period (hr.) 0.5	1.0	1.5	Clearing time	Digestion period (hr.) 0.5	1.0	1.5	Clearing time
	(g)	Hide substance		(per cent)*	(min.)	Hide substance		(per cent)*	(min.)	Hide substance		(per cent)*	(min.)
I	0.5	47.65	47.70	47.85	30	47.40	47.60	47.55	13	46.80	47.75	47.75	15
	1.0	47.30	47.50	48.05	35	47.95	47.80	47.60	16	47.10	47.70	48.00	24
	1.5	47.35	47.75	47.95	39	47.40	47.50	47.10	18	47.10	48.00	47.75	26
II	0.5	43.70	43.90	43.90	18	43.75	44.00	43.95	10	44.10	44.25	44.05	11
	1.0	43.80	43.90	43.80	21	43.90	43.95	43.80	12	44.10	44.20	44.10	13
	1.5	43.80	43.80	44.15	19	43.70	43.75	43.50	14	44.00	44.20	44.10	14
III	0.5	70.70	70.65	70.80	20	70.50	70.95	71.00	9	70.65	71.15	71.25	13
	1.0	70.30	70.70	70.60	26	69.65	70.30	70.65	15	70.55	71.05	71.05	18
	1.5	70.40	70.70	70.80	29	70.20	70.40	70.60	16	70.40	71.00	71.10	24

*Each value is the mean of two determinations.

obtained for leathers II and III than for leather I, while the catalysts and weights of specimen had no significant effect on precision. Since the results obtained from a 0.5 gram specimen are no less precise than those from the larger specimens, and since the 0.5 gram specimen offers definite advantages in distillation and titration, its use is recommended.

The leathers are apparently not all digested with the same ease. Sample II seems to be the most easily digested, as the results for the shortest and longest periods are about the same. Sample III appears most difficult to digest, since the last half hour of digestion resulted in an increase in value for nitrogen over that found for the next shorter period. This behavior will be mentioned again in the next section.

(3) Comparison of three catalysts using different digestion mixtures

The conclusion that mercuric oxide is the most efficient of the three catalysts with a digestion mixture containing 8 grams of potassium sulfate and 20 ml of sulfuric acid would not necessarily be true with other proportions in the digestion mixture. Hence an experiment was performed in which each of the three catalysts was used in each of the three digestion mixtures, containing 4, 8, and 16 grams of potassium sulfate, respectively, with 20 ml of sulfuric acid.

The specimen of leather weighed 0.5 gram for each determination. The concentrations of the catalysts were the same as in the previous experiment, except that selenium was reduced to one per cent of the sulfate-selenium mixture; this was necessary to keep the selenium concentration below the recommended maximum of 0.25 gram per determination [5]. Digestion periods were 2 hours with copper sulfate and one hour with selenium or mercuric oxide.

Temperatures of the boiling digestion mixtures were observed and in each case agreed within a degree or two with the temperatures given in Table 1.

The results, presented in Table 4, again show that mercuric oxide reached the highest values of all three leathers. Selenium yields distinctly lower values, with copper sulfate intermediate. This indicates that mercuric oxide can safely be used at the higher temperatures resulting from greater concentrations of potassium sulfate, while the use of selenium causes failure to recover the nitrogen completely. Mercuric oxide accelerates the digestion much more than copper sulfate. An analysis of the variance of the data presented in Table 4 is given in the appendix together with comments on the interpretation of the analysis.

5. Comparison of Catalysts in Digestion of Amino Acids and Acetanilide

As shown above, mercuric oxide as catalyst tends to give higher values for

TABLE 4

Effect of catalysts on determination of hide substance in leathers, with different digestion mixtures.

Catalyst		$CuSO_4.5H_2O$		Se		HgO	
Leather	Wt. K_2SO_4	Clearing time	Hide substance*	Clearing time	Hide substance*	Clearing time	Hide substance*
	g	min.	per cent	min.	per cent	min.	per cent
I	4	52	46.60	23	46.80	28	46.65
	8	23	47.45	17	47.55	19	47.65
	16	15	47.50	13	46.80	11	47.95
II	4	39	43.60	15	43.75	24	43.85
	8	15	43.80	14	43.95	12	43.90
	16	10	43.65	13	43.65	11	44.05
III	4	33	70.20	20	70.15	28	70.40
	8	14	71.10	12	70.85	13	71.05
	16	11	70.80	10	70.50	9	71.20

*Each value is the mean of two determinations.

hide substance in the analysis of leathers. Though it is probable that the higher values are more nearly correct, as nitrogen could not have come from any other source than the leather, it seemed of interest to compare the same catalysts in the analysis of pure substances, the theoretical nitrogen contents of which are at least approximately known. These substances should also be such that the nitrogen in them is combined in a manner similar to that in which it is found in leather.

Some of the amino acids present in collagen were selected for this comparison. These samples, from the Eastman Kodak Company, were glycine, lysine, and aginine as monohydrochlorides, and histidine as the mono-hydrochloride mono-hydrate. In addition, National Bureau of Standards samples of acetanilide and cystine were included.

Samples weighing approximately 0.3 gram were used for the determinations. Moissture was determined by drying to constant weight in an oven at 110°C, and the corresponding corrections were made. The digestion mixture in each case was 8 grams of potassium sulfate and 20 ml of sulfuric acid. Digestion times were 0.5, 1.0, and 1.5 hours. The concenrations of catalysts were the same as those reported in Section II, 4, (2) of this paper.

Clearing time for the amino acids ranged from 5 to 10 minutes; for the acetanilide, from 11 minutes with mercuric oxide to 14 minutes with copper sulfate. Digestion temperatures were from 332 to 335°C.

The results are given in Table 5, with the theoretical nitrogen content for each material. Mercuric oxide again yields the highest values. Lysine is by far the most resistant to yielding up its nitrogen, and mercuric oxide is the only one of the three catalysts giving values close to the theoretical amount for this material after one hour's digestion. This confirms a report elsewhere in the literature [6].

TABLE 5

Effect of catalysts in the determination of nitrogen in amino acids and acetanilide

Substance	Theoretical nitrogen content	Digestion period	Nitrogen found					
			with $CuSO_4.5H_2O$ as catalyst		with Se as catalyst		with HgO as catalyst	
	per cent	hour	per cent by weight*	per cent of theoretical	per cent by weight*	per cent of theoretical	per cent by weight*	per cent of theoretical
Arginine	26.58	0.5	26.38	99.24	26.40	99.32	26.41	99.35
		1.0	26.36	99.17	26.39	99.30	26.40	99.32
		1.5	26.43	99.43	26.35	99.13	26.41	99.35
Glycine	18.65	0.5	18.51	99.25	18.52	99.30	18.52	99.30
		1.0	18.53	99.36	18.53	99.36	18.55	99.47
		1.5	18.48	99.09	18.53	99.36	18.53	99.36
Histidine	20.04	0.5	19.75	98.55	19.80	98.80	19.78	98.70
		1.0	19.75	98.55	19.72	98.40	19.77	98.65
		1.5	19.76	98.60	19.67	98.15	19.76	98.60
Lysine	15.33	0.5	12.44	81.15	13.41	87.47	14.47	94.39
		1.0	12.71	82.91	14.04	91.58	14.98	97.71
		1.5	13.64	88.97	14.52	94.71	15.10	98.50
Acetanilide	10.36	0.5	10.07	97.21	10.23	98.75	10.26	99.04
		1.0	10.27	99.14	10.29	99.33	10.31	99.52
		1.5	10.32	99.62	10.27	99.14	10.33	99.72
Cystine	11.65	0.5	11.55	99.15	11.53	98.97	11.55	99.15
		1.0	11.52	98.89	11.50	98.72	11.56	99.23
		1.5	11.53	98.97	11.47	98.46	11.55	99.15

*Each value is the mean of two determinations.

An analysis of variance of precision of the duplicate values (lysine excluded), whose averages are given in Table 5, shows no significant difference in precision between the results obtained with any of the three catalysts or between the results obtained with the five pure compounds.

In this connection it should be pointed out that mercuric oxide generally gave the highest and most accurate results for the pure compounds, as well as for the leathers studied, and it also gave as precise results as the other two catalysts for both classes of material.

III. Distillation

The ALCA method [7] permits the use either of standardized hydrochloric or sulfuric acid or of boric acid as the absorbent for the ammonia in the Kjeldahl distillation. The use of boric acid saves time as it does not require any standard base for the titration of excess acid, nor does it require accurate measurement of the amount of solution used as absorbent. Boric acid has been extensively studied for this purpose since it was first proposed [8]. It has been shown to give good agreement with the distillation and titration using strong mineral acids [9, 10, 11, 12]. A concentrated solution, 4 per cent, is re-

quired for best results. Fifty ml of such a solution will retain ammonia equivalent to 95 mg of nitrogen [13]. The temperature of the absorbent should preferably not exceed 40°C [16], in order to prevent loss of ammonia. When kept in pyrex glass, the boric acid solution is stable for at least six months [14].

Air bubbling through the boric acid solution does not cause a significant loss of ammonia when the boric acid concentration is 0.9 per cent or more [15]. Since appreciable quantities of air pass through the solution only at the beginning of the distillation, when the boric acid concentration is 4.0 per cent, and since the concentration is lowered only to 0.8 per cent when 200 ml of water have been distilled, no error should occur from this source.

Two sources of error may easily be encountered, however. They are the entrainment of alkaline spray in the distillate [16] and the loss of ammonia, associated with poorly-fitting rubber stoppers [17]. The first can be prevented by some sort of baffle plate in the lower part of the connecting bulb thus retaining a small amount of boiling water in the bulb during distillation. This water prevents alkali spray from reaching the upper tube. Stainless steel screens form efficient baffles [18]. In the absence of special baffles, a loose plug of steel wool inserted in the lower tube of the connecting bulb effectively eliminates alkali spray entrainment. This was used in the determination reported in this paper. However, the steel wool decomposes and must be frequently replaced. Care must be taken that it does not form a crust, blocking the tube.

The entrapment of condensate between the rubber stopper and the neck of the distilling flask may sometimes cause low results, as some ammonia is apparently retained in the space and not swept out. Errors form this source are generally no greater than the experimental error of the titration, but occasionally a much larger error, as much as 1 per cent of the total titration value, may occur.

Such errors may be avoided by using spherical ground glass connections or by specially matching the rubber stoppers with the flasks for close fit, and wetting the surface of the stopper before insertion. In a series of determinations in which the only variable was the use of rubber stoppers or glass connections, there was indicated a slightly higher precision in favor of the glass connection. The standard deviation in ml of titrant, calculated from 12 determinations with glass connections, was 0.029, from 17 determinations with rubber stoppers, 0.043. However, the difference would justify glass connections only for the most precise work, because of the considerable increase in cost of the apparatus, and because the size of the sperical joint is not accomodated in the ordinary Kjeldahl digestion racks without modification. Rubber stoppers, matched with the flasks and moistened before inserting, were used in the measurements reported here.

IV. Titration

One of the reasons for the slow acceptance of the boric acid method seems to have been the difficulty in finding a satisfactory indicator for the titration. The ALCA method specifies methyl orange (methyl red is required for hydrochloric or sulfuric acid absorbent). Bromphenol blue has been suggested as more suitable [18], but neither indicator is quite satisfactory [10]. Mixed indicators such as methyl-red- methylene blue [19], methyl red-tetrabromophenol blue [20], and methyl red-bromcresol green [21], [22], have been suggested.

1. *Indicators*

The color changes of six indicators were compared in this study. They were: methyl orange, 0.1 per cent aqueous solution; methyl red, 0.1 per cent aqueous solution; bromcresol green, 0.1 per cent solution in 95 per cent ethanol; methyl red (3 parts) with methylene blue (2 parts), each 0.1 per cent solution in 95 per cent ethanol; methyl red (1 part) with bromcresol green (5 parts), each 0.1 per cent solution in 95 per cent ethanol; and methyl purple [23], a commercially prepared solution containing methyl red and a dye.

The methyl orange shows its most pronounced color change at a pH about 4.4, while all other indicators change most rapidly at pH values between 4.8 and 5.1. These values were observed by titrating 250 ml of 0.8 per cent boric acid in a 400 ml beaker, in ordinary daylight, with 0.05 *N* sulfuric acid and measuring the pH with a Fisher titrimeter and a Beckman pH meter.

The principal reason for the unsatisfactory performance of methyl orange may be seen from examination of the titration curves in Figure 1. In this experiment, 300 ml of aqueous solution containing 10 ml of 0.2 *N* solution of ammonium sulfate, 10 ml of 0.0835 *N* sodium hydroxide, and different amounts of boric acid, as shown, were titrated with 0.1 *N* sulfuric acid. For solutions corresponding to the conditions of the Kjeldahl titration, i. e., in the neighborhood of 50 ml. of 4 per cent boric acid, the pH of the end point lies between 4.5 and 5.5. Since methyl orange shows its most vivid color change below this range, its end point does not lie on the steepest part of the curve, and hence more acid is needed to effect a given degree of color change than with the other indicators.

Each of the three mixed indicators gave a color change more readily perceptible at the end point than that produced with either methyl red or bromcresol green alone. No difference was noted that would make any one of the three mixed indicators greatly preferable over the other two. The authors happen to prefer the methyl red-methylene blue mixture.

2. *The Effect of Boric Acid Concentration on the Titration*

The titration curves in Figure 1 also illustrate the effect of boric acid concentration on the titration of ammonia. From these curves it is seen that the sharpness of the endpoint (drop in pH value per unit volume of acid added

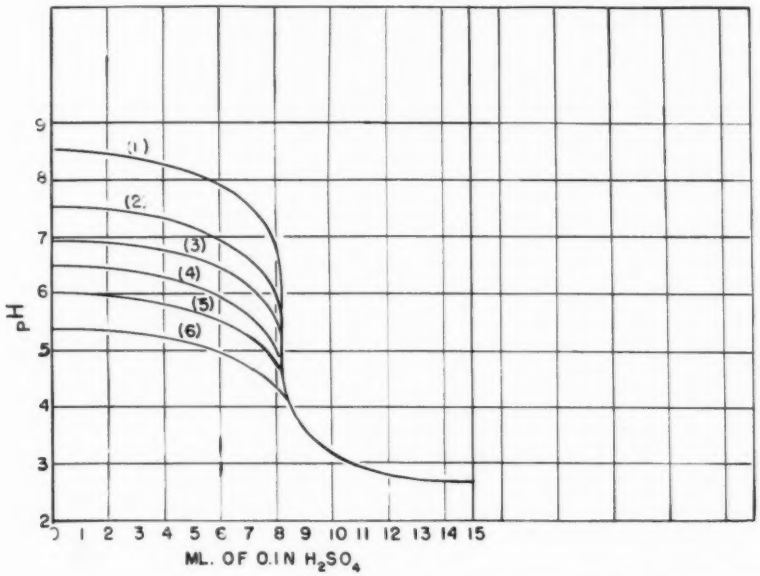

FIGURE 1.—Titration curves of NH_4OH in aqueous solutions containing various amounts of H_3BO_3. The numbered curves were obtained by titration of these corresponding solutions:

(1) 300 ml aqueous solution containing no H_3BO_3, 0.835 mNH_4OH.
(2) " " " " " 25 ml 4% " " "
(3) " " " " " 50 ml 4% " " "
(4) " " " " " 100 ml 4% " " "
(5) " " " " " 150 ml 4% " " "
(6) " " " " " 200 ml 4% " " "

near the point of inflection) decreases with increasing concentration of the boric acid.

Hence it is advantageous to use a sample weight requiring the minimum amount of boric acid. As already mentioned, it has been found that 50 ml of 4 per cent boric acid will safely absorb and hold 95 mg of nitrogen as ammonia. This is equivalent to the nitrogen present in 0.53 gram of a specimen consisting of 100 per cent hide substance. If a sample weighing 0.5 gram is used, and the standard acid is 0.1270 *N*, each 0.1 ml represents 0.2 per cent hide substance. As one drop of 0.05 *N* acid produces a readily visible change in the color of the mixed indicator in the absorbing solution, it should be rather easy to match end-points in routine determinations within 2 drops of 0.1270 *N* acid, corresponding to an error not exceeding 0.2 per cent hide substance, and, with care, even this error could be reduced. When the sample is known to contain less than 50 per cent hide substance, as in most vegetable-

tanned leathers, one-gram samples may be used without increasing the concentration of boric acid.

The use of 50 ml of boric acid has the further advantage that, when diluted to 250 ml with distilled water, the pH value of the solution is very close to the most sensitive end-point of the mixed indicators, thus minimizing the end-point correction. The smaller sample of leather is, of course more easily digested and gives less foaming during the early part of the digesting.

3. *Effects of Concentration of Ammonium Sulfate and of Carbon Dioxide on the Titration*

Two other variables in the solution to be titrated are the concentration of ammonium sulfate, which depends on the amount of ammonium titrated, and the concentration of carbon dioxide absorbed from the air. The possible effects of these on the titration were studied by conducting titrations of boric acid solutions containing different amounts of these substances. To these solutions, each containing 25 ml of 4 per cent boric acid and 10 ml of 0.08 *N* sodium hydroxide, were added 10, 20, and 50 ml, respectively, of 0.2 *N* am-ammonium sulfate. Each was diluted to 300 ml and titrated with 0.1 *N* sulfuric acid. The effect, if any, of the concentration of ammonium sulfate was less than the experimental error of the titration.

To study the effect of carbon dioxide, three solutions containing 25 ml of 4 per cent boric acid, 10 ml of 0.2 *N* ammonium sulfate, and 10 ml of 0.08 *N* sodium hydroxide were diluted to 300 ml with three portions of distilled water treated as follows: (1) freshly boiled; (2) exposed to laboratory air for several days; and (3) saturated with carbon dioxide by bubbling a stream of the gas through it for 15 minutes. On titrating with 0.1 *N* sulfuric acid, it was found that the solution saturated with carbon dioxide showed a less definite end-point, but that there was no appreciable defference between the carbon-dioxide-free solution and that in equilibrium with the laboratory air.

It is concluded that, under the conditions likely to be encountered in the Kjeldahl titration, the effects of concentration of ammonium sulfate and of carbon dioxide will be negligible.

V. Discussion of Factors Pertinent to the ALCA Method

1. *Precision of Different Steps in the Procedure*

Table 6 shows the standard deviations calculated at different stages of the Kjeldahl procedure, as well as for the complete analysis of six pure compounds and the three leathers studied. The large standard deviation for lysine is in keeping with the difficulty encountered in recovering the theoretical amount of nitrogen, as pointed out in the discussion of Table 5. An inspection of the standard deviations in Table 6 reveals that leathers II and III can be analyzed for hide substance with approximately the same precision as pure compounds. Since leather I differs from leather III only in

grease content, and since the precision of results from leather III is significantly better than that of leather I, it may be concluded that the grease in Army upper leather can have a significantly adverse effect on precision.

TABLE VI

Standard Deviations in the Kjeldahl Determination of Hide Substance. Values are based on the two longer digestion periods for each catalyst. Data on all three specimen sizes are included for each leather.

Step or operation	No. of determinations	Standard deviation, all catalysts
		(per cent hide sub.)
Standardization of acid or titration	6	0.02
Distillation and titration	6	0.09
Analysis of arginine	12	0.17
Analysis of glycine	12	0.13
Analysis of histidine	12	0.15
Analysis of lystine	12	1.98*
Analysis of cystine	12	0.10
Analysis of acetanilide	12	0.15
Analysis of Leather I	36	0.22
Analysis of Leather II	36	0.12
Analysis of Leather III	36	0.13

*For HgO catalyst, the standard deviation, based on four determinations, was 0.38.

2. *Digestion of the Specimen*

The use of a sample weighing only 0.5 gram has definite advantages in the digestion as well as in the distillation and titration. The smaller sample hastens the digestion and reduces foaming in its early stages. As shown above, the smaller sample permits the use of only 50 ml of 4 per cent boric acid solution as absorbent, thus adding to the convenience and precision of the determination. There is no particular gain in precision in using a specimen as large as 1.4 grams, as specified by the ALCA method. If the ground leather is passed through the Wiley mill twice and thoroughly mixed, 0.5 gram is quite sufficient.

Mercuric oxide as the catalyst gives a more rapid digestion than does copper sulfate, and yields better recovery of nitrogen than does selenium. It requires one brief additional step, the addition of a reagent to destroy the mercury-ammonia complex before distillation, but this does not require great care, and there is still a large net saving of time. A suitable digestion mixture for a 0.5 gram sample is 20 ml of sulfuric acid and 8 grams of powdered potassium or sodium sulfate containing mercuric oxide in the proportion of 7 grams of the oxide to 100 grams of the sulfate.

3. *Distillation and Titration*

The volatility of mercury and some of its compounds is a factor to be considered in connection with the distillation. When appreciable amounts of chlorides are present, some mercuric chloride is deposited in the neck of the flask during digestion. However, this does not seem to affect the results. Mercuric oxide as catalyst has been objected to on the ground that it volatilizes and amalgamates with the block tin condenser tubes commonly used in the Kjeldahl apparatus. When an all-glass apparatus was used in this laboratory, the fact that volatilization of the mercury occured was indicated by slight turbidity of the boric acid solution, provided that distillation was started immediately after addition of the sodium thiosulfate solution. But if the flasks were allowed to stand for 5 to 10 minutes with occasional shaking after the addition of thiosulfate, such turbidity never occurred. If the latter procedure is followed, then, it seems safe to assume that volatilization of the mercury will be negligible.

Boric acid as the absorbent is thought preferable to the standard hydrochloric or sulfuric acid. It requires only one standard solution and only one accurate measurement in the determination. It is a stable solution and can be stored at least 6 months. Precautions against carbon dioxide contamination become unnecessary. No objectionable feature of the boric acid method was observed in this study.

4. *Indicator.*

The methyl orange indicator specified by the A.L.C.A. method is much less suitable for this titration than any of several mixed indicators. Such a mixed indicator as 0.06 per cent methyl red and 0.04 per cent methylene blue in 95 per cent ethanol solution gives a much more sharply defined end-point, and one that corresponds more closely to the stoichiometric point as shown by electrometric titration curves.

VI. Recommended Modifications of the ALCA Method

In view of the results obtained in this investigation, the following modifications of the ALCA method are suggested:

1. The weight of specimen should be 0.5 gram. The leather should be prepared by passing twice through a Wiley mill with a 4-mm screen, being throughly mixed after each pass.

2. The digestion mixture should consist of 20 ml of sulfuric acid and 8 grams of a mixture containing 7 parts of yellow mercuric oxide to 100 parts of sodium or potassium sulfate by weight.

3. After cooling and dilution of the digestion mixture, 25 ml of an 8 per cent sodium thiosulfate pentra-hydrate solution should be added to precipitate the mercury, and the flask allowed to stand for 5 to 10 minutes with occasional shaking before proceeding with the distillation.

4. The absorbent solution should be 50 ml of 4 per cent boric acid solution, with 10 drops of a mixed indicator containing 0.06 per cent methyl red and 0.04 per cent methylene blue in 95 per cent ethanol solution.

5. The distillation apparatus should include a scrubber-type connecting bulb with steel wool or screen to prevent entrainment of non-volatile alkali in the distillate. Special care should be taken that rubber stoppers fit the flasks tightly, and are wetted before insertion.

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VIII. Appendix

Analysis of variance of data in Table 3.

Source of Variance	Degrees of Freedom	Sums of Squares	Mean Squares	Variance Ratio (F)	
Total	53	765,438	——	——	
Within duplicates	27	44.5	1.63	——	
Between duplicates	26	765,394	——	——	
Leathers	2	764,678	382,339	——	
Catalysts	2	123	61.5	49.2	(significant)
Digestion mixtures	2	268	134	107.2	"
Leathers x catalysts	4	26	6.5	5.2	"
Leathers x digestion mixtures	4	176	44	35.2	"
Catalysts x digestion mixtures	4	113	28	22.4	"
Leather x catalysts x digestion mixtures	8	10	1.25		

The analysis shows that the effects of leathers, catalysts, digestion mixtures, and the three two-factor interactions are all significant. The large variance of the leathers is, of course, due to the difference in per cent hide substance of the three samples, and is included only to permit calculation of the other items. That significant differences in the results can be caused by using different catalysts or different digestion mixtures might have been observed by an inspection of Table 4. The three two-factor interactions in the table above, however, show in addition that the effect of either the catalyst or the digestion mixture is not the same for all leathers. Nor is the effect of the catalyst the same for all digestion mixtures. The agreement between the mean square of the 3 factor interaction (1.25) with that corresponding to the variability within duplicates (1.63) indicates that no appreciable source of variance exists except those considered in this analysis.

ABSTRACTS

Amino Acid Analysis. By G. R. Tristan. *Chem. and Industry*, No. 53, S 868 (1950). Various methods for the determination of amino acids are critically discussed.

A Simple Trap for Use with a Water Pump. By D. Geoghegan. *Chem. and Ind.*, No. 5, 94(1951). A simply constructed water trap has proved of service in preventing water entering a filtering flask, or other apparatus, being evacuated by a water pump. It consists of a short piece of wide glass tubing, such as the neck from a broken 500-ml. flask, fitted with single-holed rubber bungs at each end; the upper bung holds a 10-ml. pipette, or other similar type of bulb tube, with a Bunsen valve attached to its taper. The lower bung carries a short piece of glass tubing, one end pushed up to emerge just below the level of the seating; the other end is connected with the pump. The valve slit is made with a razor

blade in one side of the rubber tubing parallel with the taper of the pipette. This arrangement allows sufficient clearance for the valve to function, and prolong the life of the tubing by preventing complete collapse on closure. The pipette bulb serves to catch any slight leakage of water which may pass through the valve during any violent fluctuations of pressure. It serves, also, as an indicator of the efficiency of the valve, any retained water being sucked away when the pump recommences working.

The Evolution of Tanning Procedures With Polymeric Anhydrous Phosphates (Coriagen Tanning). By Kurt Lindner. *Das Leder*, **1**, 203 and 233 (1950). Over 15 years ago Lindner observed that acidified aqueous solutions of Calgon, sodium hexametaphosphate, would change hide to a leather-like substance and a patent was obtained for tanning with polymeric metaphosphoric acid or its alkali salts. The phosphate salt was called Calgon in Germany and the United States but the tanning preparation was named Calgon in the United States and Coriagen in Germany. Wilson in the United States discovered the tanning action of these phosphates at about the same time. Developments in phosphate tanning are reviewed. The author summarizes the present situation as follows: The tanning compounds are high polymeric phosphoric acids, especially those of the metaphosphoric acid type. Technical products contain appreciable amounts of higher polymers than hexametaphosphate. "True" tanning occurs in the acid region. The polymetaphosphoric acid and the amino groups of the skin form salt type bonds. At optimum pH value (2.35) and maximum take-up, the ratio of amino nitrogen to phosphorus is 1:1. The maximum take-up is 9.3 grams of HPO_3 per 100 grams of hide substance. At optimum pH, polyphosphate treatment is more of a tannage than a pickle because (1) the phosphate leather is resistant to putrefaction, (2) it does not acid-swell on washing, (3) the phosphate does not wash out, (4) the shrinkage temperature is 63–65° as compared with 38° for the pickled skin.

Salts, especially chlorides, adversely affect combination; therefore before tanning, skins should be washed until salt free and addition of salt during tanning should be avoided. In the presence of appreciable amounts of neutral salt or at higher pH values polyphosphate acts partly as a tannin and partly as a pickle. In the region from pH 6 to pH 7 polyphosphate causes strong neutral salt swelling of the skin. At about pH 9 all tendency for combination with the skin ceases. Polyphosphate tannage greatly improves vegetable tanning. Even in strong liquors the vegetable tannin cannot overtan the grain layer. It is not yet known whether the vegetable tannin gradually replaces the polyphosphate or whether the amino groups of the hide protein are completely or partially masked by polyphosphate so that the combination with vegetable tannin occurs in another manner. Pretannage of chrome leather with polyphosphate results in firmer leather of increased tensile strength, increased Cr_2O_3 content and smoother grain. Smaller amounts of chrome than normal can be used without lowering leather quality. I.D.C.

Sulfide Stains and Discolorations on White Hide. By G. Joerss. *Das Leder*, **1**, 257 (1950). In sulfide lime liquors there are sharply defined, strongly colored bluish-black specks of iron sulfide on the skins and also weaker, less sharply defined blue areas caused by iron salts and sulfide. (Schultz *J.A.L.C.A.* **23**, 356) found little or no discoloration if the hides were treated with alkali before they came in contact with sulfide and that discoloration was greater on poorly cured hides. The iron contents of various components of a lime liquor are approximately as follows: Hide 0.01 per cent; hair (5-10 per cent of the hide) 0.03 per cent; sodium sulfide concentrated (60 per cent Na_2S) 0.1 per cent; sodium sulfide crystalline (30 per cent Na_2S) 0.003 per cent; low iron lime, 0.1 per cent; other limes 1.0 per cent; and water 0.1 milligram per liter. A lime liquor might therefore contain either 2 grams of iron from 2 kilograms of concentrated or 0.12 grams of iron from 4 kilograms of

crystalline sodium sulfide, 5-50 grams of iron from 5 kilograms of lime, 12-13 grams of iron from 100 kilograms of hide and 0.5 grams of iron from 500 liters of water. Only a small proportion of the iron is from the sulfide. Laboratory experiments were made on calfskins with lime pastes and liquors, comparing the staining by concentrated and crystalline sodium sulfide, by good and poor curing of the skins, and of liming for 24 hours in a straight lime before putting them in a sulfide lime versus starting them in a sulfide lime. The results showed that the iron content of the sulfide had no influence on the skin properties and was not responsible for the sulfide discoloration. Allowing the sulfide solution to settle and adding only the clear solution to the lime did not alter the results. Poorly cured skins were discolored more than well cured ones. Staining was decreased or prevented by a preliminary liming in straight lime. I.D.C.

Hide Damages and Their Control. By Franz Margold. *Das Leder*, **1**, 281 (1950). A brief description with illustrations is given of the common skin parasites. These are (1) ticks, (2) mites which may be divided into burrowing mites (*Acarus*), sucking mites (*Psoroptes*) and scale eating mites (*Chorioptes*), and (3) two types of lice, *Anoplura* and *Mallophyga*. Dry hides are attacked by beetles and moths. Formerly cresol preparations, pyrethrum and derris extracts were used to protect animals but some of the new products such as DDT (dichloro-diphenyl-trichloromethylmethane) are more effective. DFDT (difluoro-diphenyl-trichloromethylmethane) is much more poisonous to warm blooded animals than DDT. Both DDT and Gammexane (hexachlorocyclohexane) are valuable additions to the list of insecticides for controlling parasites. In times when hides are so valuable the following control measures should be taken: (1) periodic spraying or washing all animals with a 1 per cent gammexane solution at intervals of about 4 months as a preventative against mites, ticks, and lice; this treatment will also kill 60-70 per cent of the grubs; (2) spray stalls to kill flies and other vermin that disturb the animals and spread disease; (3) treat at once with gammexane, skins that are to be dried; (4) provide means in hide houses and tanneries for fumigating dry hides overnight; or (5) if they cannot be fumigated, spray them with gammexane emulsions, using at least 0.5 gram of active ingredient per square meter of skin and fumigating the room every 4 weeks. I.D.C.

Determination of Chromium in Chrome Leathers Containing Aluminum. By A. Küntzel and Hildegard Kuhtz. *Das Leder*, **1**, 287 (1950). Oxidation and decomposition of the ash of leather tanned with chrome and aluminum salts is incomplete with chlorate fusion mixture (2 parts potassium chlorate, 3 parts potash, 5 parts soda). Borax mixture consisting of equal parts of borax, soda, and potash is preferable. The ash from 2 grams of leather should be mixed with 4-5 grams of borax mixture and fused for 30 minutes. The fused material should be dissolved in hydrochloric acid and reduced with a little ethyl alcohol. Aluminum and chromium are precipitated together and weighed as the hydroxides after which chromium is determined iodometrically. Direct precipitation of aluminum from the fused mixture (with chrome as chromate) is less exact because of the small aluminum content. Decomposition of either leather or its ash with perchloric-sulfuric acids is as satisfactory as fusion with borax mixture and makes possible the determination of silicic acid. I.D.C.

The Preparation, Evaluation and Use of Synthetic Tannins. By J. A. Sagoschen. *Osterreichische Leder-Zeitung*, **4**, No. 19, 6; No. 20, 6 (1949). The development of syntans is reviewed. Syntans must be completely soluble in water, 70-90 per cent should salt out, and they should have a tanning value of at least 50 and a combining value of at least 30. The ash content of replacement tannins should not exceed 10 per cent with maxima of 0.1

per cent Fe_2O_3, 1 per cent CaO, and 0.5 per cent MgO or Al_2O_3. The various uses of syntans for tanning, decreasing insolubles, assisting in other tannages and neutralizing mineral tannages are briefly described. No replacement syntans have been made in Austria to date, only auxiliary syntans. I.D.C.

Sweetened Chestnutwood Extract. Anon. *Osterreichische Leder-Zeitung*, **5**, No. 23, 473 (1950). In 1935, when quebracho extract could not be imported, Italian technicians developed a substitute known as sweetened chestnut wood extract. This was made by treating chestnut extract so that it resembled sulfited quebracho in astringency, acid content, molecular dispersion, pH value, etc. It produces light colored, light-fast leather. Yields of sole leather of 62 per cent or more are obtained as compared with 57 per cent with quebracho. It is still being used by Italian tanners for sole, upper, and sheep lining leathers. I.D.C.

PATENTS

Acylated Protein and Method for Making Same. U. S. Pat. 2,525,792. W. G. Gordon, R. W. Jackson, Philadelphia, and A. E. Brown, Washington, assignors to U. S. of America. Appl. July 8, 1947. A process of preparing a protein derivative which is completely soluble in warm, dilute aqueous alkali, comprising reacting an aqueous alkaline solution of a protein material with the chloride of an aliphatic higher fatty acid containing 8 to 18 carbon atoms, precipitating the formed acylated protein derivatives by acidifying the resulting solution, and recovering the acylated protein derivative.

Leather Skiving Machine or Splitter. U. S. Pat. 2,527,811. R. W. Hall, Cincinnati, Ohio, assignor to the Randall Co., Cincinnati, Appl. Sept. 13, 1948. A mechanism of the adjustable type for various thickness of product.

Leather Substitute. U. S. Pat. 2,530,441. H. A. Reinhardt and W. T. Harrison, Longmeadow, Mass., assignors to Biglow-Sanford Carpet Co., Thompsonville, Mass. Appl. Aug. 3, 1945. A sheet material comprising a homogenous continuous body of a compressed thermoplastic vinyl chloride—vinyl acetate resin and a plasticizer therefor, a sheet of an open-weave woven cloth embedded within said continuous body of resin, and a mass of individual reinforcing unwoven crimped rayon staple fibers 2-6 inches long and 10-35 deniers diameter extending through the openings thereof and randomly disposed vertically and horizontally and individually embedded in and permeating said continuous body of resin at both sides of the cloth, said resin constituting the major part by weight of said sheet, and a pigment distributed through said continuous body of resin.

Dehairing Machine. U. S. Pat. 2,531,209. W. Gilbert, Richmond Hill, N. Y. Appl. Nov. 30, 1946. A dehairing machine for fur bearing skins comprising a box having two contacting plucking rollers, one of which has a resilient gripping surface and the other a series of spaced gripping jaws having gripping surfaces parallel with the axes of the follers, a guard plate beneath said rollers with a narrow slot beneath the contacting surfaces of the rollers, means for driving one of said rollers, means for adjusting one roller toward the other, a rotatable supporting guide rod for the skin being operated on, movable toward and away

from the slot in the guard plate, foot actuated means for moving said guide rod, the slot in the plate being so narrow that the skin cannot be pushed into contact with the contacting rollers.

Manufacture of Animal Glue Jellies. U. S. Pat. 2,531,715. T. A. White, Jackson Heights, N. Y., assignor to National Starch Products, New York. Appl. Apr. 28, 1948. An animal glue composition comprising animal glue, a reducing sugar acting as a plasticizing medium and a selected ammonium compound the ammonium radical of which acts to reduce or inhibit the resinification of the glue composition, the ammonium compound being selected from the group consisting of ammonium chloride, ammonium nitrate, ammonium thiocyanate and ammonium lactate, the said ammonium compound being in the proportion of from a fraction of 1 per cent to 20 per cent by weight of the dry animal glue in the composition.

Leather Splitting Machine. U. S. Pat. 2,532,398. H. Fehlmann, Courtelary, Switzerland. Appl. July 6, 1948. A splitting machine of the band cutter type.

Machine for Smoothing or Ironing Leather, Particularly Shoe Sole Leather. U. S. Pat. 2,532,601. A. Bucek, Otrokovice, Czechoslovakia, assignor to Bata, Zlin. Appl. Aug. 27, 1947. In a bridge rolling machine including a carriage, a pressure exerting device mounted on the carriage comprising spring biased toggle levers and vertically movable thrust plates actuated by said toggle levers, and a vertically movable working roll having bearings engaged by said thrust plates, the arrangement of the bearings of the working roll so as to be completely separate from the pressure exerting device of the machine and to be freely movable up and down along a path and in a space confined by the walls of the carriage frame and the thrust plates of the toggle levers of the pressure exerting device, the latter being mounted as an adjustable unit in the carriage frame in such a way that the clearances between the bearings of the working roll and the thrust plates of the toggle levers of the pressure exerting device are variable as required, within the limits of a free movement, not loaded by the said pressure exerting device, of the working roll.

Leather-Like Material. U. S. Pat. 2,533,976. M. C. Teague, Ridgewood, N. J., assignor to U. S. Rubber Co., New York. Appl. Mar. 1, 1945. A leather-like multi-ply shoe upper material having elastic properties and a textile inner face and a plastic outer face, and formed of two fabrics bonded together by a layer of rubber lying therebetween and which normally holds both fabrics in a condensed condition so that these fabrics will stretch between 8 and 25 per cent in one direction and less than 5 per cent transversely to such direction, at least one of said fabrics being knitted and having firmly adhered to its condensed outer surface a stretchable tough layer of a heat softening vinyl resin that is about 0.02 inch thick, to thereby provide a flexible and stretchable composition sheet material that will give good wear without scuffing, sagging, or cracking and without needle cutting when embodied in the upper part of shoe.

Method of Extraction of Tannic Acid from Sumac Leaf. U. S. Pat. 2,537,510. G. Carrara, Milan, Italy. Appl. Feb. 17, 1948. In a method for the recovery of a low specific gravity light colored tannin from sumac leaves the steps of extracting the pulverized leaves with water by percolation and at a temperature not exceeding 50°C. until about 50 to 55 per cent of the tannin contained in the leaves is removed as an aqueous solution, concentrating the same to about 10-12° Be., cooling to about 0° C., further concentrating to about 28-30° Be. and extracting with ethyl acetate, the ratio of the acetate to the extract being about 1.2 to 1.0.

Production of Artificial Protein Threads, Filaments, and the Like. U. S. Pat. 2,542,803. R. L. Wormell, Coventry, England. Appl. Nov. 25, 1949. In a process for the production of protein threads by extruding a solution of the protein through a jet into a setting medium, and treating the resultant thread in at least one aqueous bath containing formaldehyde to render the thread resistant to the action of water, the steps of treating the thread with an aqueous solution in which chloral is dissolved, whereby the protein is softened and the thread becomes elastic, and stretching the thread at least 50 per cent while it is in the elastic state.

Production of Artificial Protein Fibers. U. S. Pat. 2,541,804. R. L. Wormell, Coventry, England. Appl. June 20, 1950. A process for the production of protein fibers soluble in dilute alkaline solutions comprising extruding an alkaline protein solution into a coagulant bath containing at least one metal salt to coagulate the protein, stretching the resultant thread at least 50 per cent, rendering the stretched thread resistant to cold water by treatment with an aqueous bath containing chloral and drying the thus hardened thread, the entire process being effected in the absence of formaldehyde.

Artificial Chamois Skin and Method of Making the Same. U. S. Pat. 2,540,906. G. W. Overton and B. E. Spencer, Freeport, Ill., assignors to Burgess Cellulose Co., Freeport, Ill. Appl. June 5, 1947. A sheet of cellulose regenerated from viscose, and having its broad outer surfaces more dense than the interior.

Method of Solubilizing Keratin. U. S. Pat. 2,542,984. C. H. Binkley, Berkeley, Cal., assignor to U. S. Govt. Appl. Feb. 25, 1949. A process of preparing a high molecular weight solubilized keratin derivative having the property of forming a gel when a hot aqueous-alcohol solution thereof is cooled, comprising heating a reaction mixture containing a keratin-containing material, a neutral, normally-liquid, water-soluble alcohol consisting of carbon, hydrogen, and oxygen, water, and an acid at a temperature of about from 100°C. to 150°C., said alcohol and water being present in the proportion of about from 0.25 to 3.0 volumes of alcohol per volume of water and said acid being present in sufficient quantity to give a final pH of about from 2.5 to 4.0 at the conclusion of the reaction, thereby to produce said keratin derivative.

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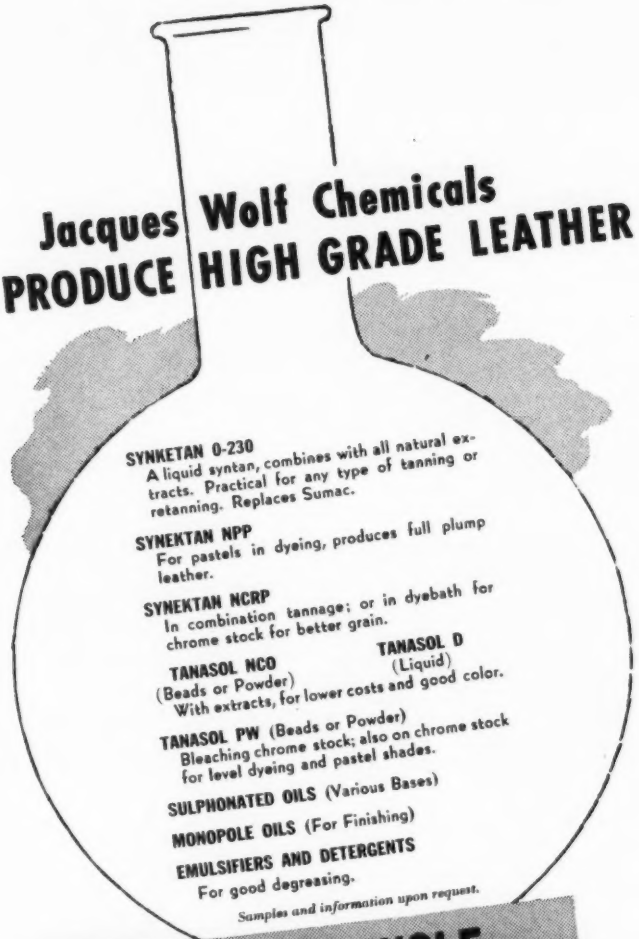

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